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THE FISH LIVER OIL INDUSTRY

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United States Department of the Interior

United States Department of the Interior, J. A. Krug, Secretary
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THE FISH LIVER OIL INDUSTRY

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HISTORICAL BACKGROUND

Cod liver oils were in use as general medicinals as early as 1840. The cod liver oils from the English, Norwegian, and Newfoundland fisheries were, for years, the chief sources of supply. Pharmaceutical houses, interested in the procurement of better quality oils, gradually improved the conditions for selection and care of the livers and the technique of processing and refining. Early in the twentieth century, chemists established the fact that the beneficial factors in fish liver oils were the vitamins A and D.

Then, in 1929, it was reported that the oil from the livers of Atlantic halibut had a higher vitamin A and D content than cod liver oil. Within two years, pharmaceutical companies were purchasing livers in the Pacific coast halibut fishery. Shortly thereafter they began to buy tuna livers also. As a result of the stimulated interest in sources of supply, sablefish, lingcod, and rockfish livers were next found to be of value. Subsequently, grayfish livers, and halibut and sablefish viscera were processed for vitamin oils.

In 1937, livers from the soupfin shark were first processed in California. After a preliminary period, in which the types of gear most suitable for the capture of the soupfin shark were being worked out, this fishery assumed more and more importance. The combination of high vitamin A content and high oil content peculiar to the soupfin liver was particularly valuable as war conditions over the world began to interfere with the normal movement of fish liver oils from foreign sources.

The entry of the United States into active participation in the war stimulated the fish liver oil industry to renewed heights of activity and production. Governmental purchases of vitamin A oils for Lend-Lease and the increased demand for the lower potency oils in the expanded animal and poultry feeding program soon reduced reserve stocks of vitamin A to a low ebb. Then too, the American public was becoming vitamin conscious at a time when purchasing power was high; therefore the volume of sales of vitamin oils and capsules for human use also constituted a large and continuing demand on the industry.

Fortunately, there have been improvements in fish-liver processing, in fish-oil concentration, in efficiency of fishing methods, and in care of the fish livers by fishermen and dealers, all of which, in combination with the increased effort to bring to port every possible pound of vitamin-bearing material, enabled the United States to serve, in effect, as the vitamin A supplier to the world in this emergency.

The literature contains many highly technical reports of isolated segments of vitamin oil processing, such as the characteristics of specific vitamin oils, or a method of analysis; but no unified description of the many ramifications of the industry has been available. This report is designed to bring together into one publication the widely scattered information about this relatively young industry that has grown from a humble beginning to international economic importance in so short a time.

Table 1, Annual Production of Fish Liver Oils in the United States, 1934-45, in the appendix, shows the increase in the vitamin oil production in the last decade. Table 2, Relative Importance of Fish Liver Oils in the United States from Principal Species in 1943, indicates the approximate present sources of our vitamin oils.

Fish livers, especially those from cod, halibut, the tunas, and other gadoid and percomorph fishes, were for many years one of the principal sources of the vitamins D for human and animal nutrition. In recent years, however, with the advent of the synthetic vitamins D derived from activated ergosterol and activated 7-dehydro-cholesterol, these sources of natural vitamin D have become less important. There is still a demand in the pharmaceutical trade for cod liver oil and percomorph liver oil. Many purchasers of fish livers and fish liver oils do not, at present, pay a premium for the vitamin D content since they are primarily interested in the vitamin A content and will pay only on the basis of vitamin A activity per gram of oil. If a specified vitamin D content is required in subsequent uses of the vitamin oils, the synthetic product, usually derived from animal sources, is blended into the oil in the desired amount.

For these reasons the discussion of the vitamin oil industry in this report has been almost exclusively limited to the vitamin A field. There are in the context brief descriptions of the assay methods now used for the estimation of the vitamins D; and in the Appendix Table 5 "Vitamin D Content of Oils from Fishery Sources", there is a compilation of data for forty-four species of fish.

CLASSES OF LIVERS WITH RESPECT TO OIL CONTENT AND VITAMIN A POTENCY

Fish livers, for purposes of this report, are divided into three categories: (1) high oil content-low vitamin A potency, (2) low oil content-high vitamin A potency, and (3) high oil content-high vitamin A potency. Fish viscera will be treated as a separate but closely allied cagegory. This segregation of vitamin-bearing materials into arbitrary groups will facilitate the discussion of processing methods. Since there is some overlapping of the characteristics, a definition of terms will be made.

High oil content-low vitamin A potency livers are those containing from 60 to 75 percent of oil by weight, with each gram of oil having a vitamin A potency of 500 to 20,000 U. S. P. units. Examples of this class are the livers from cod and grayfish.

The low oil content-high vitamin A potency class includes those livers containing from 4 to 28 percent oil by weight with each gram of oil having a vitamin A potency of 25,000 to 600,000 U. S. P. units. The livers from sablefish, halibut, lingcod, rockfish, and tuna are examples of this class.

Fish livers which do not logically fall into either of the two previous classes have been arbitrarily grouped in the high oil content-high vitamin A potency class. There are two subdivisions within this class: (1) those livers containing from 45 to 75 percent oil by weight with each gram of oil

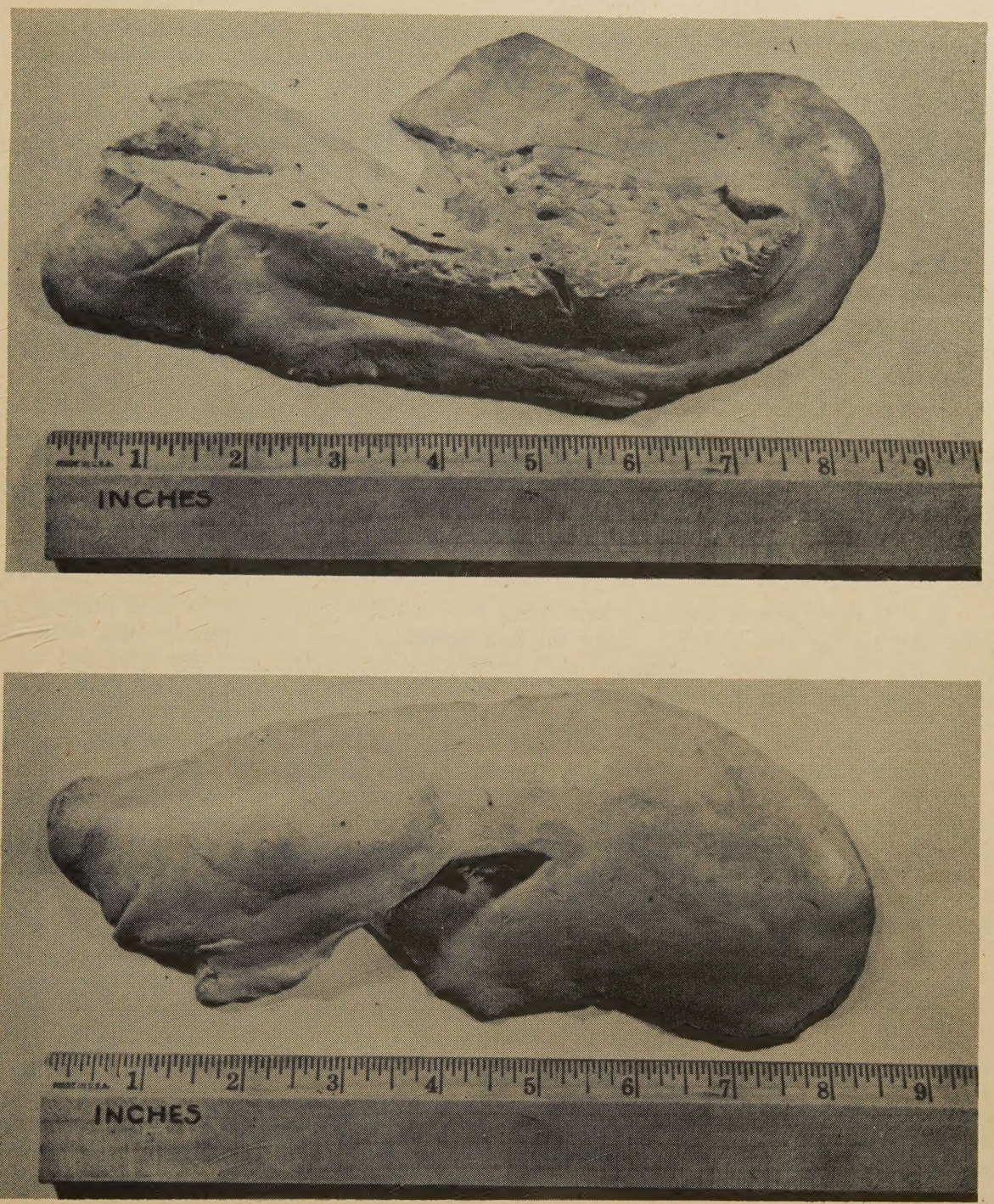

Figure 1. Halibut (Hippoglossus hippoglossus) liver, weight 179 grams, from a fish weighing approximately 25 pounds (11.4 kilograms). Liver color is normally light tan with greenish cast. Texture is medium firm. Upper photo is dorsal view, showing liver as it would appear in the fish looking down at the back and toward the anterior portion of the fish. Note the characteristic outline, with clefts and truncated pyramid shape. Lower photo is ventral view, showing liver as it would appear looking down at the belly of the fish and toward the anterior portion. Note deep cleft on lower side and rounding shape of liver.

having a vitamin A potency of 20,000 to 200,000 U. S. P. units, and (2) those livers containing from 30 to 75 percent oil by weight with each gram of oil having a vitamin A potency of 0 to 340,000 U. S. P. units. The livers from the soupfin sharks are examples of the former subdivision. Livers from female soupfin sharks may contain oil having only 20,000 U. S. P. units of vitamin A per gram, while livers from male soupfin sharks have yielded oil at the 200,000 unit potency level.

The second subdivision of high oil content livers includes those from miscellaneous species of sharks. The liver from the basking shark is an example of the very low potency type. Oil recovered from the liver of this shark usually does not contain in excess of 300 U. S. P. units of vitamin A per gram. The hammerhead shark is an example of the other extreme in this class. A Florida processor has reported tests on hammerhead-shark livers in which the oil contained 340,000 U. S. P. units of vitamin A per gram. In Tables 3 and 4 of the appendix there are tabulated the content of oil by weight and the content in vitamin A per gram of oil for the other miscellaneous sharks. The content of oil by weight does not vary so much from one species to another, but the vitamin A per gram of oil does vary throughout the range mentioned above.

The term viscera usually includes the entire contents of the abdominal cavity excepting the liver. Some buyers specify that the gonads and stomach should also be removed. Commercial processing has been largely limited to viscera from halibut and sablefish.

RELATIONSHIP OF OIL CONTENT AND VITAMIN A POTENCY TO CHOICE OF EXTRACTION METHOD

Since the vitamin A in fish livers is generally considered to be associated to some degree with the liver tissue, the choice of a processing method is somewhat dependent upon the relationship of oil content and vitamin A potency. If a liver has a high oil content of relatively low potency, there is less justification for an elaborate or expensive extraction procedure, and the large volume of oil present can be expected to act as an oil-solvent medium for the vitamin A present.

As the oil content decreases the protein present becomes more and more important as a factor in the determination of processing technique. The oil is more closely held by the protein; and, since there is less oil present to extract the vitamin A, some means must be employed to assist in the extraction or to destroy the power of the protein to retain the oil and vitamin A.

Fish viscera usually have a very low oil content, and the tissue tends to hold the oil and vitamin A even more firmly than in the case of most fish livers. Processes designed to handle livers economically have, as a rule, not been profitable in handling viscera.

In the appendix, a series of tables will be found which contain data on miscellaneous subjects pertinent to the use of fish livers and viscera as sources for vitamin oils. The data are classified as follows:

Table 3, Miscellaneous Data on Fish Livers and Viscera of Commercial Importance in the United States and Canada.

Table 4, Miscellaneous Data on Fish Livers and Viscera.

Table 5, Vitamin D Content of Miscellaneous Oils from Fish Livers and Viscera.

PROCESSING METHODS

High Oil Content-Low Vitamin A Potency Class

Steaming of Cod Livers

For many years cod livers have been processed by direct cooking with steam. The equipment and procedure employed have been improved and altered to conform to changing fishery conditions and to market demands for a better quality vitamin oil. Some schooners and trawlers which remain at sea for protracted periods still use a small liver boiler to recover an excellent quality medicinal cod liver oil. For small-scale operations on shore, an inexpensive method has been suggested by Labrie and Fougere (1). The apparatus is essentially a percolator with steam as the extracting medium. Livers are placed in a perforated inner cylinder mounted on the steam pipe fastened to the water reservoir below. The apparatus may be placed on a stove as a source of heat. Steam formed above the water in the reservoir is distributed through the central pipe to the livers in the perforated cylinder. Occasional stirring of the liver mass facilitates the cooking process and the subsequent liberation of the oil. The oil separates during the cooking process, flows out of the inner cylinder through the perforations, collects in the outer cylinder, and is then drained through a cloth filter bag into a storage receptacle. The apparatus is said to recover as much as 80 percent of the oil contained in cod livers without recourse to pressing the residue. A good grade of oil can be obtained if fresh livers are used and proper sanitary precautions are taken. Approximately 15 gallons of cod livers may be processed per 5-hour period in an apparatus having over-all external dimensions of 36 inches by 16 inches and a cooking cylinder measuring 24 inches by 13 inches.

Modern shore plants utilize the steam processing method with more refinements and on a larger scale. Since the development of satisfactory methods of preservation, livers have been received in good condition from the larger boats; and both the total production and the proportion of medicinal grade cod liver oil have been materially increased.

The livers to be used for medicinal grade cod liver oil should be very fresh, unbruised, and free from gall bladders. Only livers from the

(1) Labrie, H., and H. Fougere, 1937. New Cod Liver Oil Extractor. Fish. Res. Bd. Canada Prog. Rept., Gaspe Exptl. Sta. Bull. 21, pp. 6-8.

cod (Gadus morrhua Linne'), (often described as Gadus callarias), and other species of the family Gadidae (such as haddock and hake) are permitted by the United States Pharmacopoeia. If the livers are to be cooked with live steam, they are placed in large tanks into which steam is injected to bring the livers to a boil. Norwegian regulations state that livers may be heated to 185-192° F. (85-90° C.). The cooking process is continued until the disintegration of the livers frees the oil. Some producers skim off the oil from the cooker tanks into settling vats, but the better practice is to put the oil through a centrifugal purifier to remove suspended solids and moisture. If the oil is to be sold as de-stearinated cod liver oil, it must be cooled slowly to about 35° F. (2° C.), to allow the stearines to crystallize out, and then be passed through a pressure filter. The stearines are retained on the filter cloths, and the de-stearinated oil may then be packaged for shipment.

Some processors cook the livers in steam-jacketed kettles instead of by the direct-steam method. Some means of agitation is employed to facilitate disintegration, and the livers are heated only to 158-167° F. (70-75° C.). The separation of the liberated oil may be accomplished by either of the methods described above.

An additional yield of oil, suitable for stock feeding, can be obtained by further treatment of the chum, or residual solids, from the initial cooking. After the liberated oil has been skimmed off, the chum is recooked. The oil is then pressed out of the chum in a hydraulic press. The remaining press cake is also of some value as a stock feed and is sometimes dehydrated for longer-term preservation.

Cold Flotation of Cod Livers

At Rimouski, Quebec, a cold flotation process has been used. The first prerequisite of this process is that the livers be firmly coagulated by the preservatives used; in this particular instance, a patented preservative, consisting in part of volatile aldehydes, is employed on the boats or at the shore stations along the coast. The preservative is said to limit the formation of fatty acids and, at the same time, to destroy the enzymes which would normally cause deterioration of the liver. Enamel-lined, steel drums are supplied for the storage and shipment of the livers to the processing plant.

At the plant the livers are drained of excess liquid and inspected on a conveyor belt as they move to the series of grinders that reduce them to a fine pulp. The cod liver oil is separated from the pulp by means of a flotation process. The oil has a protein and water content of approximately one-half of one percent. This water, and any of the preservative material carried over, is removed by application of heat in the subsequent continuous dehydration stage. A relatively low temperature is used, and the destruction of vitamin A is lessened since the exposure to heat is for only about seven seconds. Suspended fine protein materials are removed from the oil by filtration. In order to conform to trade practice, the oil is then cold-cleared to meet the 32° F. cold test. The oil is stored under nitrogen to protect the vitamin A content.

Steaming of Grayfish and Shark Livers

On the Pacific Coast the steaming process has been employed to recover vitamin oils from grayfish (dogfish) livers. The livers are usually ground to facilitate the separation of the oil from the tissue. Live steam is introduced into processing tanks charged with the ground livers. Some additional mechanical agitation is required to insure rapid and uniform cooking of the charge. After the liver tissue has been thoroughly washed by

Figure 2. Grayfish (Squalus suckleyi) liver, weight 225 grams, from fish weighing approximately 5 pounds (2.3 kilograms). Liver color is gray black. Normal color variations are from light cream to gray black. Note characteristic mottling or network pattern and clefts. Texture is soft. Upper photo, dorsal view; lower photo, ventral view.

the freed oil to extract any vitamins present, the oil may be allowed to separate by gravity, but separation in a three-phase or sludger-type centrifugal is preferable. In some plants there may be an additional centrifuging operation to insure the removal of small amounts of suspended solids and moisture from the oil. All Pacific Coast processing plants are equipped to handle liver oils by the centrifuge separation method.

This method has been used to process shark livers in those cases where the oil content is rather high (50 percent) and the potency is low (8,000-15,000 U. S. P. units per gram of oil), e. g. mud-shark livers in Alaska, and miscellaneous shark livers in Florida.

After the initial processing of high oil content-low vitamin A potency material, such as grayfish livers, by alkali digestion, the amount of vitamin A remaining in the water discharge from the centrifuge is not sufficient to warrant further extraction by means of a "wash oil". However, with livers of low oil content but high vitamin A potency, the initial separation of the oil leaves a considerable amount of vitamin A in the aqueous phase, which may be profitably recovered by means of a series of extractions with an added oil to collect the vitamin A before the water is thrown away.

The alkali process enables the plant operator to produce a sparkling clear oil, but it is possible that oils so produced are not as stable because of the removal of substances that protect the vitamin A from oxidation. However, some authorities believe that the losses of some of the natural antioxidants during the alkali digestion process are more than compensated for by the lowering of the free fatty acid content. These authorities reason that excessive free fatty acids, acting as pro-oxidants, do more actual damage to the vitamin A oil than the natural antioxidants present could counteract. Usually an oil that has a free fatty acid content considerably in excess of one percent will be alkali refined before being used, and any natural antioxidants present will be, at least in part, removed by this process. These brief comments are included here to point out the status of present information. The question is by no means definitely answered at the present time.

Modifications of Steaming Method

Harrison and Hamm (2) in the course of their investigation into methods for the extraction of vitamin A from grayfish (dogfish) livers found that oil freed from the livers without the digestion process had considerably less vitamin A potency than the composite sample and that it was possible to remove as much as 80 percent of the assayed oil content of the livers by grinding the raw livers and removing the freed oil by means of a basket centrifuge. The potency of the oil so obtained was 1,850 U. S. P. units of vitamin A per gram compared to a potency of 5,060 U. S. P. units of vitamin A per gram for the total oil recovered from the composite sample by solvent extraction. By any of the usual steaming, acid, or alkali digestion methods,

(2) Harrison, R. W. and W. S. Hamm, 1941. Extraction of vitamin A from Dogfish livers. Pacific Fisherman, 39, No. 9, 37-39.

the residue from this centrifuging operation could then be processed to recover an oil considerably more concentrated with respect to vitamin A content. For example, by acid digestion, these workers obtained an additional amount of oil equivalent to 13.5 percent of the assayed oil content and at a potency of 15,200 U. S. P. units of vitamin A per gram.

A somewhat different approach to this same matter of removal of a large portion of relatively lower potency oil without the removal of a proportional amount of the total vitamin A content of the livers was reported by Bailey (3). He investigated the problem from the standpoint that the addition of suitable chemicals to the ground livers would cause the protein portion of the tissue to coagulate. In the resultant contraction, a part of the contained oil would be freed without including the equivalent portion of the vitamin A content of the entire liver sample. From livers so treated in one series of experiments, approximately one-half of the oil was set free within a short time. The oils so freed were decanted from the residual solids, and the residue was steamed. The cooked material was then separated from the second lot of oil by filtration and centrifuging. A third extraction of oil was made on the residue by means of solvents. In the three separate lots of oil extracted from the original lots of ground livers, there was obtained a potency differential at each stage. The oil released by the chemical coagulation of the protein had only one-third to one-half the vitamin A potency of the oil subsequently released from the residue by steaming. When the residue that had undergone both chemical coagulation and steaming was subjected to solvent extraction, an additional 2 to 10 percent of the total oil was recovered; and this fraction had four to five times as much vitamin A potency per gram as the first oil fraction, which had been recovered by chemical coagulation alone.

The use of chemicals was also tried out to a limited extent on a larger scale at the suggestion of Bailey. A saturated solution of calcium chloride was added to tanks of ground livers, and the mass was agitated for approximately 15 minutes until uniform mixing had taken place. After the agitation was stopped, there was a gradual separation of the oil from the coagulated protein materials. This oil was then drawn off, heated to 180-190° F. (82-88° C.) with steam, and the moisture removed in an oil purifier-type centrifuge. The residue was cooked with steam and the oil separated from the solids in the sludger-type centrifuge. For grayfish (dogfish) livers the separation due to the action of calcium chloride was of the order of 80 percent of the total oil recovered. The potency of this oil was 2,500 compared to a potency of 7,000 U. S. P. units of vitamin A per gram from the oil extracted from the cooked residue. Mud-shark livers so treated yielded 68 percent of the oil content initially, the

(3) Bailey, B. E., 1941. Preparation of Vitamin A Oils from Dogfish Livers. Prog. Rept. Fish. Res. Bd. Can. Bull. 50, 11.

the balance of 32 percent being recovered from the cooked residue. The potencies of these oils were, respectively, 7,000 and 14,000 U. S. P. units of vitamin A per gram.

These various experimental results indicate that, at least with the group of fish livers having a higher oil content, some degree of concentration of the vitamin A present may be accomplished. There may not always be a sufficiently significant increase in the potency of the residual oil over that to be expected from normal processing technique to make up for the added cost of processing.

Figure 3. Grayfish (Squalus suckleyi) liver, weight 750 grams, from fish weighing approximately 16.5 pounds (7.5 kilograms). Color of livers varies from light cream (as shown here) to gray black. Texture is soft. Mottling shown is characteristic.

Pressure Extraction of Livers

Another method for the processing of high oil content-low vitamin A potency livers, apparently based on patent number 2,134,163 issued to Nentworth, has been used to a limited extent. The livers and dried, shredded beet pulp--a byproduct of beet-sugar manufacture--are mixed and macerated together in proportions that depend on the varying oil and water content of the livers. This mixture is then hydraulically pressed to remove approximately 90 percent of the oil originally contained in the livers. The carbohydrates of the beet pulp absorb most of the water from the liver mass

and thus promote the separation of the oil from the water and protein. The press liquors are held in tanks until the small amount of water and solids removed with the oil in the pressing operation has separated by gravity settling. These layers of solids and water are then drawn off and discarded. The oil should not contain more than 0.3 percent moisture and should preferably be heated before being transferred to storage to insure good keeping characteristics. The press cake is dried to approximately 10 percent moisture content and used for feed. This process utilizes the water-soluble vitamin content and other valuable nutritive constituents of the livers; the small residual oil content in the dried press cake also serves as a vitamin A and D supplement in the feed mixture.

Pressure Cooking of Livers

Some processors recommend that the initial cooking of livers be done in a closed vessel or retort with steam pressures of from 30 to 100 pounds. This procedure has the advantage that the enzymes are completely inactivated. In certain instances, livers so cooked have been shipped from several buying stations to a centrally located plant for processing. Livers having a high oil content are sufficiently broken down in the pressure cooker to facilitate removal of the oil without further digestion, but livers having a low oil content would require treatment by one of the additional digestion methods mentioned in the next section.

Low Oil Content--High Vitamin A Potency Class

In general, halibut, rockfish, lingcod, tuna, and sablefish livers are in the low oil content-high vitamin A potency class (although sablefish livers contain as much as 30 percent oil at times) and are all usually treated by similar methods. The oil in livers of this class is more closely held by the proteinaceous materials, so that these livers require a more elaborate process than livers of high oil content. Many companies claim that they have developed processes which they regard as valuable trade secrets. Probably these developments consist of variations in technique and procedure from the recognized methods that have been in use for several years. A suggested procedure based on the general method used in laboratory and pilot-plant scale processes will be described in some detail here. Precautions to avoid or minimize processing difficulties will also be mentioned. A few of the many processes described in the patent literature will then be briefly set forth to illustrate the general principles involved.

Digestion Methods

Alkali Digestion Process

Livers of the low oil content-high vitamin A potency class may be ground through a grinder of either the hammer-mill or food-chopper type to reduce their particle size before they are processed. This step is not needed if adequate agitation is provided during the subsequent processing

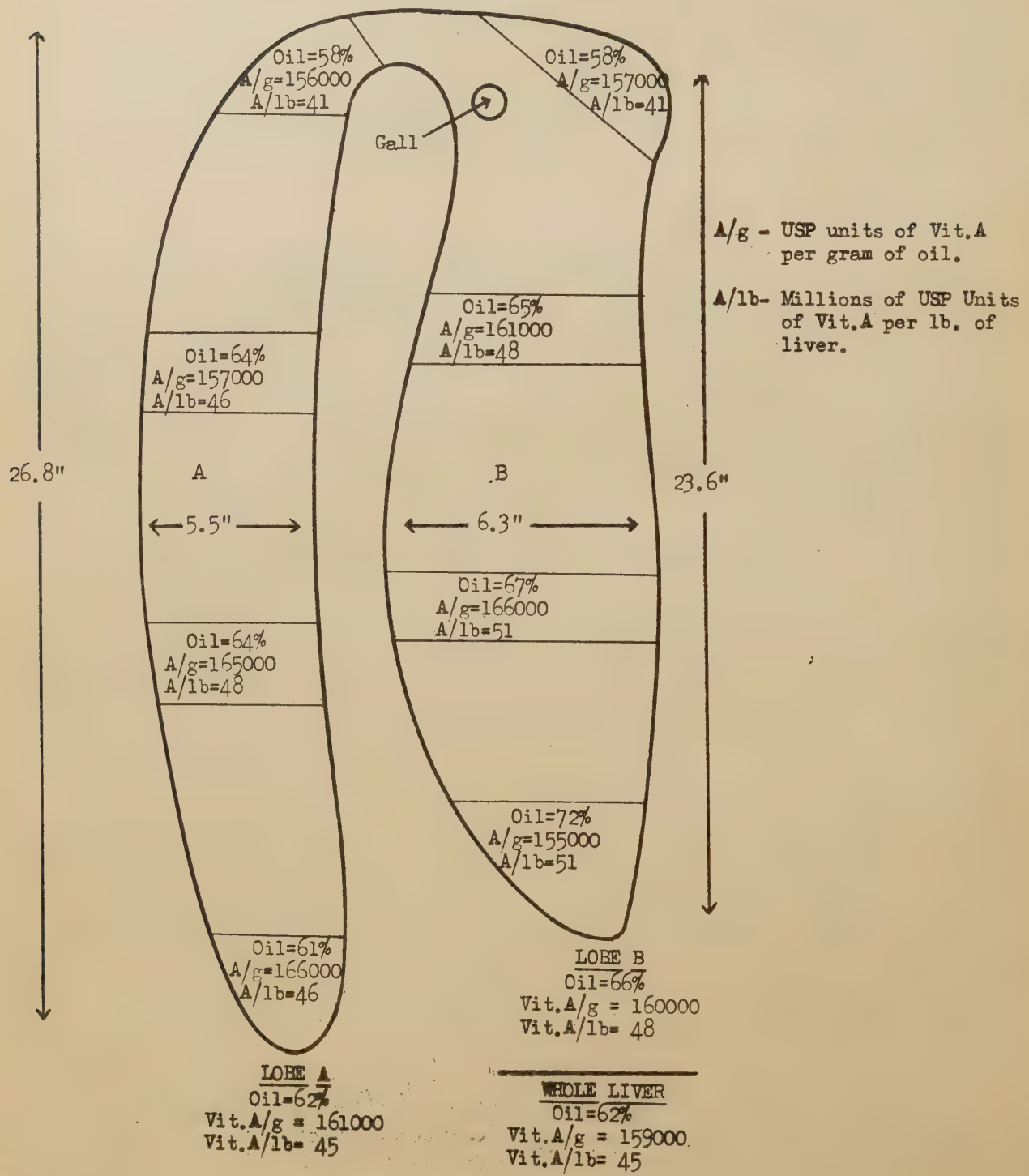

Figure 4. Distribution of Vitamin A in a Soupfin Shark (Galeorhinus zyopterus) liver.

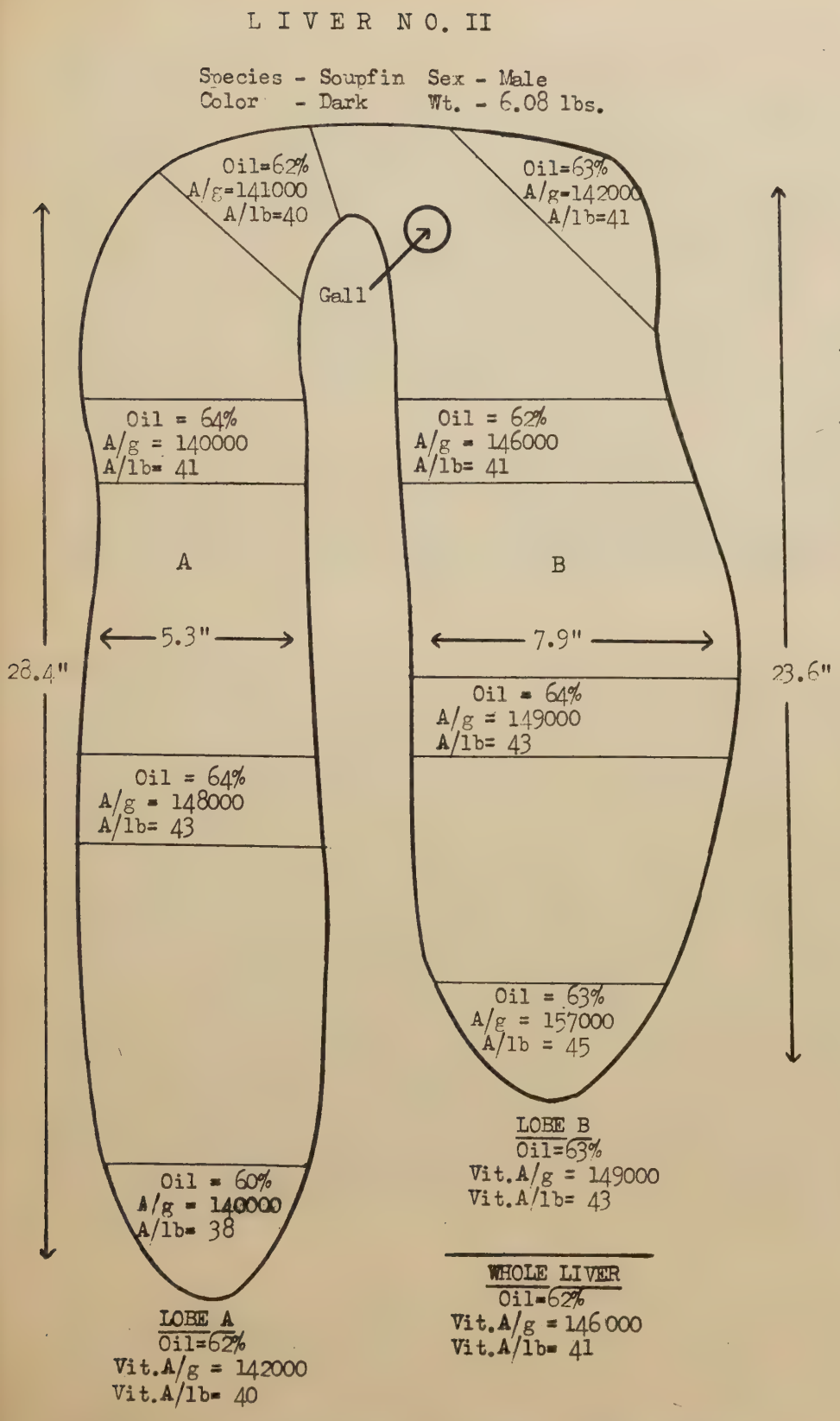

Figure 4. Distribution of Vitamin A in a Soupfin Shark (Galeorhinus zyopterus) liver.

to facilitate the even distribution of the heat and the interaction of the liver with the digestive agents. The agitation is recommended for most applications, but the type of stirrer blade, speed of rotation, etc. will vary with the particle size of livers to be processed, the time and temperature of the digestion, and with the species from which the livers are derived. Some processors introduce steam into the grinder chamber, especially if the disintegrator-type grinder is used, to drive out entrapped air and to lessen the oxidation of the oil during this period of violent mixing and mincing.

The liver containers, grinder, pipes, pump, etc. should be flushed out with water to carry any oil and particles of liver into the digestion tank. Any additional dilution of the contents of the tank, other than that from condensate in those cases where heating is by the direct steam method, should be kept within the range of one-half to one part of water to one part of liver. Although water facilitates the digestion process insofar as heat transfer, mobility, and contact of liver with digestive chemicals is concerned, any excess may lead to troublesome emulsification and absorption of vitamin A on soaps. Then, too, the capacity of the processing plant is decreased since all the liquors from the digester must be passed to the centrifugals.

If the water phase from the first such separation is saved from an oil solvent extraction or "wash oil" treatment, the volume of material to be handled should be kept at a minimum since unavoidable additional amounts of hot water will have to be used to rinse out the tanks, centrifugal, and pipe lines every time the "wash oil" treatment is employed. Often the volume of the liquor from the initial digestion is increased by one-fourth to one-half if a series of four washes is required. Obviously the capacity of the tanks employed to treat such a volume of material would have to be somewhat larger than the capacity required for the initial liver digestion.

Perhaps the simplest, and one of the most effective, means for releasing the oil and vitamins from livers of this class is by mild alkali digestion. This digestion is accompanied by the addition of one to two percent by weight of sodium hydroxide, or two to five percent by weight of sodium carbonate, followed by cooking with live steam and with suitable agitation, until the liver mass is fluid. The digestion should be carried out at approximately 180-190° F. (82-88° C.) and should be continued until the solid particles of liver tissue have been converted to a semi-colloidal, or better, to a liquid state. At this stage, the maximum amount of oil will be liberated; and no difficulties will be encountered in the centrifugal separation stage that follows immediately.

As an example of the importance of complete digestion, data collected from a commercial operation at several stages in the process may be of interest. The grayfish livers were passed through a disintegrator and pumped into the digestion tank. After a few minutes, a sample of the free oil rising to the top of the tank was taken for a vitamin A assay. The digestion was then begun, and at intervals a sample of emulsion was taken from the top of the tank and assayed for vitamin A. The potencies of the oils separated from these samples were:

Figure 5. Lingcod (Ophiodon elongatus) liver, weight 69 grams, from fish weighing approximately 12.5 pounds (5.7 kilograms). Liver color is normally dark tan with slight olive cast. Texture is very firm. Upper photo is dorsal view, showing characteristic shape, ridges, and markings. Lower photo is ventral view. Note clefts on left portion.

Free oil prior to processing	-	6,300 U. S. P. Units/gram of oil
After 20 minutes of processing	-	10,400 U. S. P. Units/gram of oil
After 40 minutes of processing	-	11,100 U. S. P. Units/gram of oil
After 65 minutes of processing	-	11,800 U. S. P. Units/gram of oil
After 90 minutes of processing	-	11,900 U. S. P. Units/gram of oil

The time required for optimum digestion will depend upon the species from which the livers are taken and also upon such other factors as the alkalinity of the digestion mixture, size of the particles, degree of agitation, and the temperature maintained. Usually at 180-190° F. (82-88° C.) grayfish livers ground through a 1/8-inch to 1/4-inch mesh disintegrator screen will be digested in approximately one hour at a pH of 8-9. The amount of alkali added should be enough to insure adequate digestion, but not enough to cause excessive soap and emulsion formation. Some companies determine the acidity of the ground liver mass and add a quantity of alkali sufficient to neutralize the free fatty acids and also to provide enough excess alkali for efficient digestion. The degree of decomposition of the livers has a bearing on the amount of alkali required for these two functions.

The liquor from the digestion tank at 180-190° F. (82-88° C.) is passed through a three-phase or sludger-type centrifugal to separate the oil in the form of an emulsion. To insure removal of all oil, the machine is set to skim into the water layer or to "skim wet". The pH of the discharged emulsion may then be suitably adjusted to promote complete recovery of the oil in the purifier-type centrifugal. When this latter centrifugal is properly adjusted and operated, the discharged oil from the purifier is substantially marketable. However, if the oil contains suspended soaps or excess free fatty acids, further refining may be necessary.

The water phase--containing the semi-colloidal particles of liver tissures, any adsorbed vitamin on the soaps, and any oil inadvertently spilled over during the centrifuging process--is usually pumped into a second tank for the "wash oil" treatment. Details of this procedure are given under the heading of "Enzyme and Alkali Digestion Process" below in this same section.

Process variations best suited to any given operating conditions are obviously legion. For example, if a processor is not particularly concerned about loss of oil as oil and wishes to use the vitamin A as an ingredient in feeding oils, he may prefer to use more alkali in the processing to facilitate the removal of the free fatty acids and to increase the degree of digestion. Conversely, soupfin shark livers, or other livers high in oil and vitamin A potency, if very fresh when processed, would require relatively less alkali for safe and satisfactory production of marketable oil. From time to time, variations within even the same species and locality necessitate alteration of processing technique for maximum efficiency of recovery. Experience previously gained in actual plant operation may be drawn on when such variations are encountered, especially if the workers have been alert and have kept notes of the procedures used in overcoming past problems.

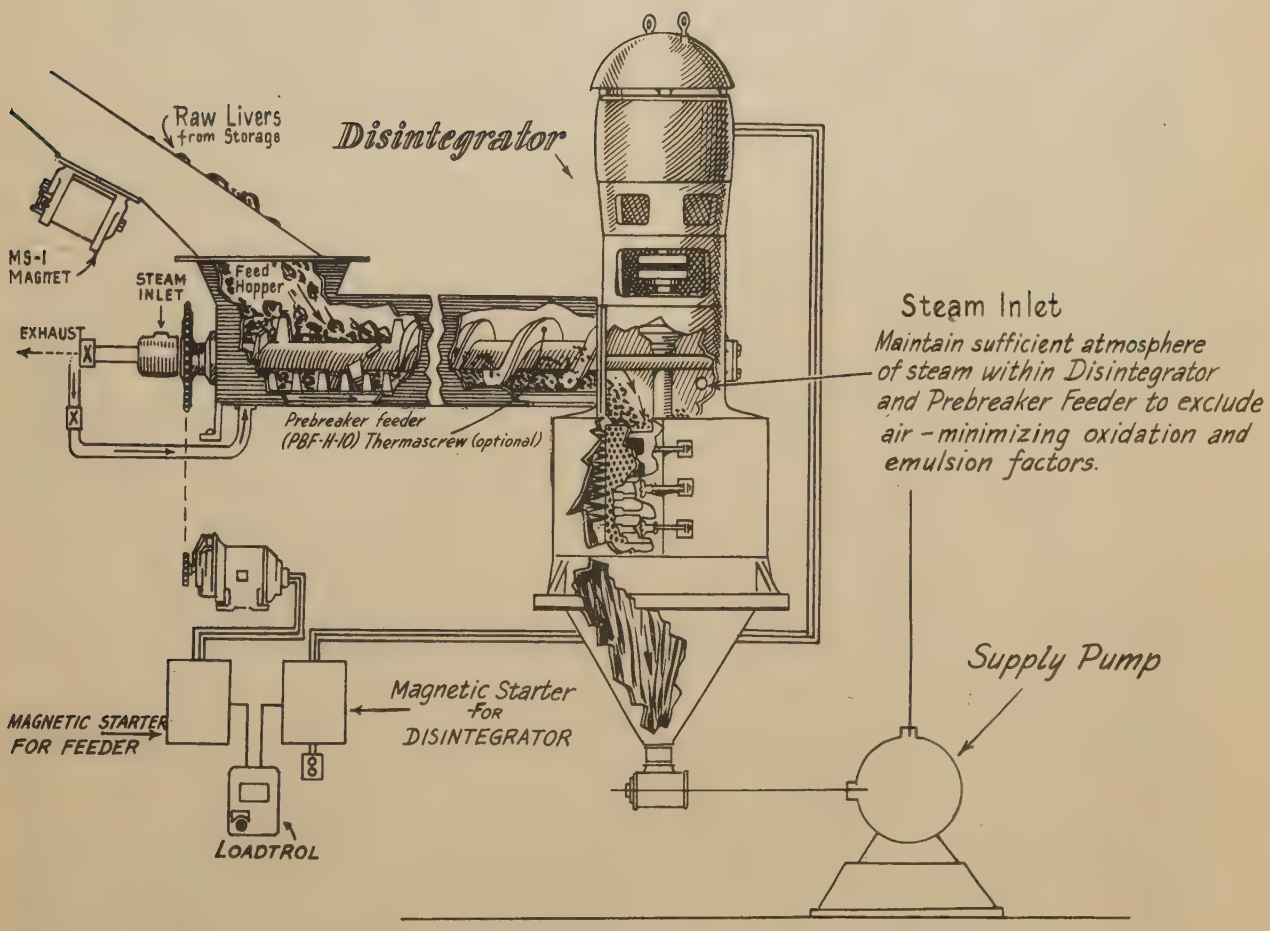

Figure 6. Sketch of liver disintegrator. (Photo courtesy Process Machinery Company.)

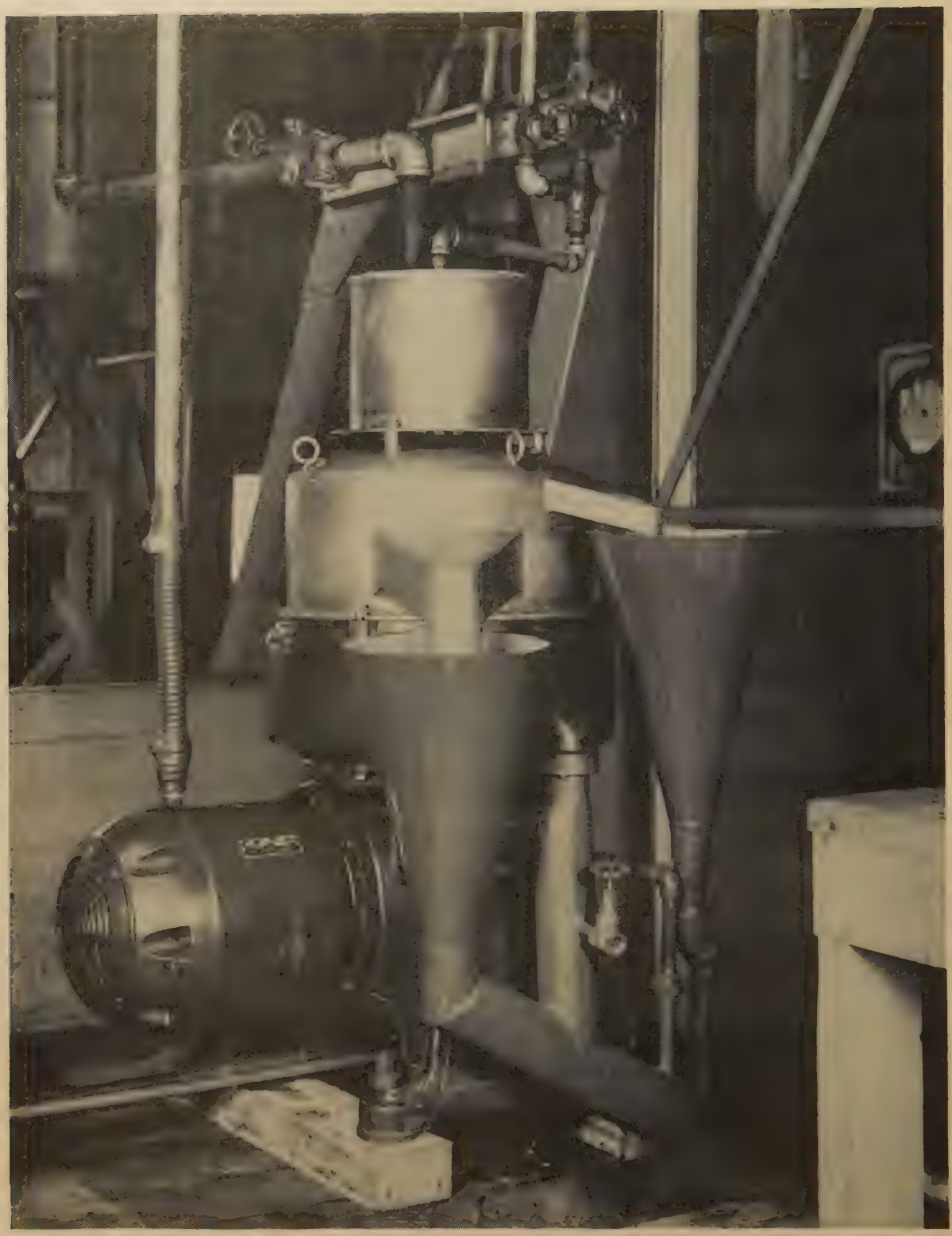

Figure 7. Three-phase, sludger-type, fish liver oil separator. (Photo courtesy of The Sharples Corporation.)

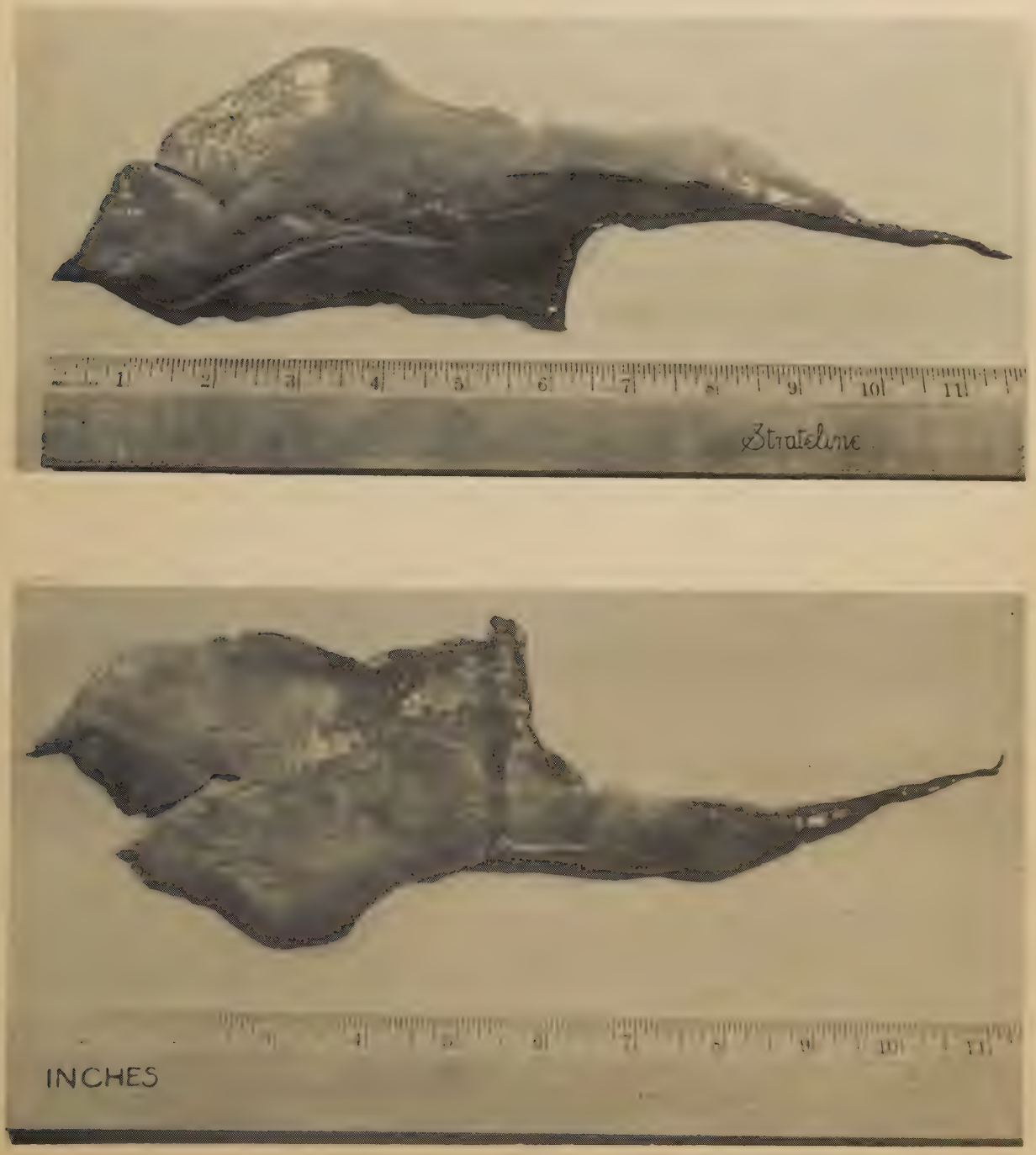

Figure 8. Rockfish (Sebastodes ruberrimus) liver, weight 103 grams, from fish weighing approximately 15 pounds (6.8 kilograms). Liver color varies within the species from dark greenish brown to cream with reddish cast. Texture is firm. Upper photo is dorsal view showing characteristic shape and markings. Lower photo is ventral view.

Patents on Digestion Processes

Young and Robinson (4) were issued patent number 2,136,481 entitled "Process of Obtaining Vitamin Containing Oils". In their process, the fish livers are first placed in a tank of hot water at approximately 180° F. (82° C.). Then sufficient alkali (sodium hydroxide) is added to neutralize the free fatty acids present. Since the percentage of free fatty acids varies with the degree of decomposition of the livers, the amounts of alkali suggested are from one to two and one-half percent of the weight of the livers. The liver mass is now digested with constant stirring at 194° F. (90° C.), for about one hour. After the digestion is completed, the agitation is stopped. The tank contents will, in the course of two or more hours, separate into an upper layer, consisting of the oil as a semi-emulsion, and an aqueous lower layer. After the latter layer has been drained off, the oil is removed from the emulsion. One method for accomplishment of this separation is to add three volumes of a five-percent saline solution to the emulsion and stir the mixture for about 15 minutes. This treatment washes out the free alkali and partially breaks the emulsion. The aqueous layer formed after the mixture has settled for two hours is drawn off, and the washing procedure is repeated once more. The washed oil emulsion is heated to 167° F. (75° C.), and then passed through a centrifugal separator.

The traces of moisture remaining in the oil discharged from the centrifuge are removed by agitation of the oil in the presence of a dehydrating agent, such as anhydrous sodium sulphate. Protection against oxidation of the oil and a simultaneous stirring action may be provided by the introduction of carbon dioxide at the bottom of the tank.

It is claimed that the oil from this process is light in color, substantially free from disagreeable taste or odor, and contains less than one percent of free fatty acids and less than one-tenth of one percent of nitrogenous material.

Herbert Hempel (5) was granted patent number 2,156,985 for a "Method of Treating Fish Livers". In this process it is recommended that the livers be ground to a smooth, fluid consistency. The digestion is then carried out the pH being maintained at 8.5 to 12.5 throughout the treatment. The weaker alkalies, such as ammonium hydroxide, tri-sodium phosphate, and borax are said to be suitable; especial emphasis is placed on the selection of materials having a buffer action to maintain the desired pH throughout the digestion process. Specific pH values are recommended to insure that free fatty acids will be neutralized and that the protein materials are substantially converted to a soluble form without undesirable hydrolysis and saponification of the liver oil. Examples are cited of the losses of oil from processing livers at pH values as follows:

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(4) Young, Ferdinand H. and Hugh D. Robinson, 1938. U. S. 2,136,481. Process of obtaining vitamin containing oils.

(5) Herbert Hempel, 1939. U. S. 2,156,985. Method of Treating Fish Livers.

at a pH of 14 - a loss of over 50 percent,
at a pH of 12.5 - a loss of about 13 percent,
at a pH of 11.5 - a loss of less than 3 percent,
and at a pH of 11 - no loss of oil.

Ammonium hydroxide is mentioned as the preferred alkali. It is used in the proportion of 166 pounds of a 26 to 28 degree Baumé solution for each 500 pounds of livers. The alkali is said to penetrate the liver mass and begin the digestion within a relatively short period. Sufficient water is then added to the charge so that the water, including the condensate from the live steam introduced to heat the mixture, constitutes about twice the volume of the livers used. A digestion period of 15 to 20 minutes at 170-175° F. (77-80° C.) is sufficient to convert the tissue into a substantially liquid form. The oil globules are released from the tissue so that the centrifugal readily separates the oil in a slightly wet state.

This wet oil is washed first with water and second with a dilute citric acid solution to neutralize and remove any remaining alkali, and then the oil-bearing layer is re-centrifuged. The washed oil may be completely dried with anhydrous sodium sulphate as described in the previous patent.

Enzyme and Alkali Digestion Process

Brocklesby and Green (6) (7) worked out a modification of the alkali digestion process by combining that method with a preliminary enzymatic peptization. According to their procedure the livers are minced and diluted with an equal volume of water. The pH is adjusted to 1.2 to 1.5 by addition of sufficient 25 percent hydrochloric acid. Commercial pepsin equal to 0.05 percent of the weight of the livers is dissolved in a little water, and the solution is added to the livers. The enzymatic digestion is continued with constant stirring for 35 to 48 hours at a temperature of 110-120° F. (43-49° C.). At the end of this first digestion period, sufficient saturated sodium carbonate is cautiously added to increase the pH to approximately 9. The temperature of the mixture is then raised to 175° F. (80° C.) and the alkali digestion is allowed to proceed for approximately one hour. Then the oil is separated by centrifugation.

When very fresh livers are processed by the alkali digestion method, considerable difficulty is sometimes encountered in the separation of the oil from the other components of the emulsion. The introduction of the enzymatic digestion step is said to minimize this difficulty, while the coincident addition of mineral acid stops the action of any fat-splitting enzymes that might be present in the livers and thus, to a large extent, prevents the formation of free fatty acids.

(6) Brocklesby, H. N. and K. Green, 1934. Fish. Res. Bd. Can. Prog. Rept., Bull. 22, 18. Methods for production of fish liver oils from livers of low oil content.

(7) Brocklesby, H. N. and K. Green, 1937. Fish. Res. Bd. Can. Prog. Rept., Bull. 33, 7. Variations in vitamin A content of liver oils in the grayfish.

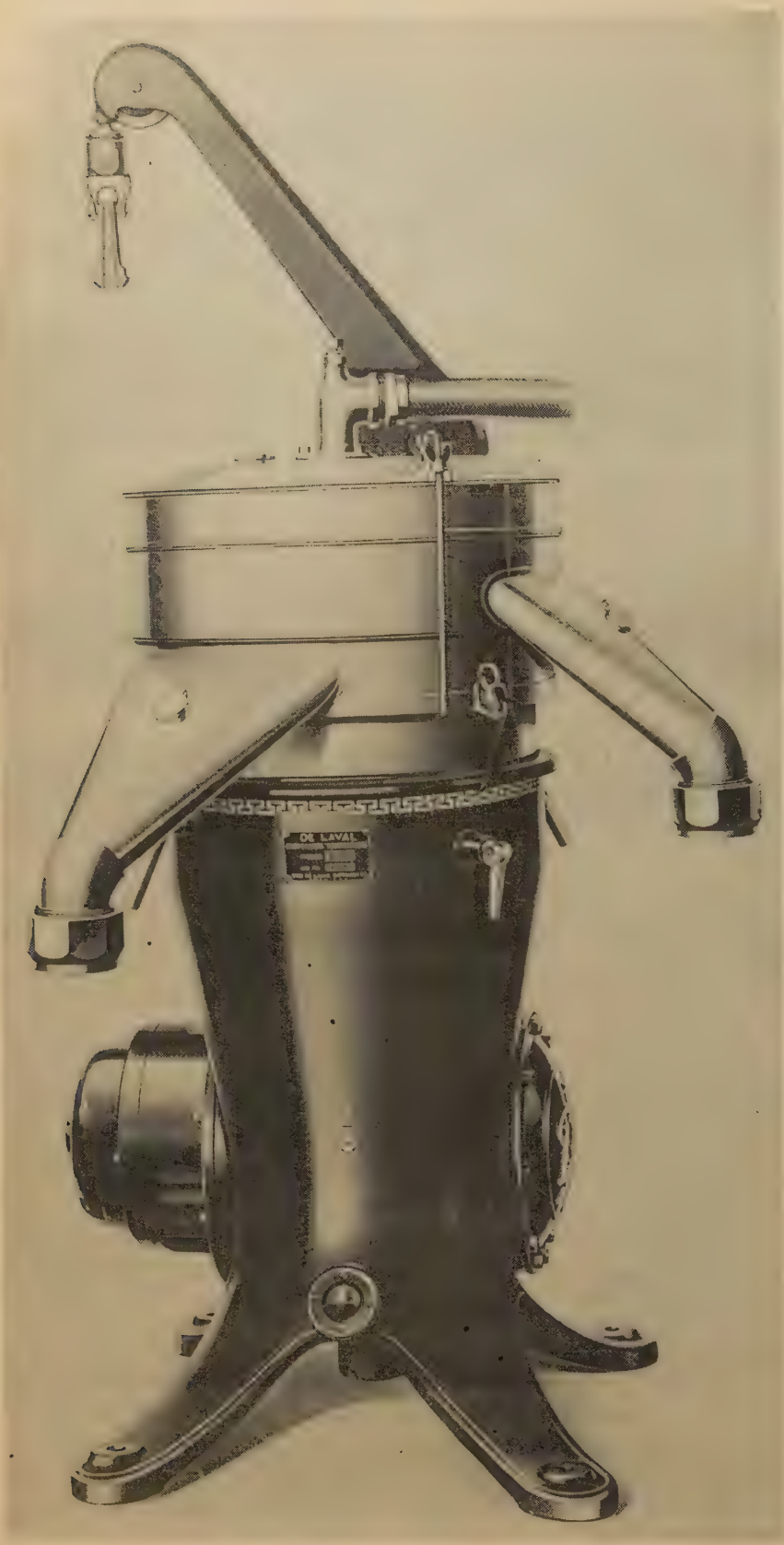

Figure 9. Fish liver oil centrifugal. (Photo courtesy De Laval Separator Company.)

Because the soaps formed during the alkali digestion often carry considerable quantities of the vitamin A into the water phase, Brocklesby and Green suggest a subsequent extraction of the aqueous discharge from the centrifugal. This discharge is mixed with a vitamin-poor, edible oil, heated to 175° F. (80° C.) and stirred to allow the added oil (or wash oil) to extract the vitamins from the soap solution. The wash oil is then centrifuged off. The oil extraction process is repeated with a second lot of oil. These washings may be repeated, with additional quantities of vitamin-poor oil, as many times as may be justified by the value of the vitamins so recovered.

A counter-current system of wash oils may be used wherein a low potency oil may be built up to a higher potency level. For example, the wash oil from the fourth extraction is added as the third extraction oil of the next batch of livers. This same oil is recovered and used as a wash oil for the second extraction of a third lot of livers. Then for the fourth lot of livers, this oil is used as the first wash oil. The amount of wash oil used may be calculated so that in the course of the counter-current treatment the vitamin A content will increase to a point where the wash oil can be profitably refined and sold as a vitamin-bearing oil. At

the same time the percentage of vitamin A remaining in the liver mass can generally be economically reduced to almost zero.

There are several disadvantages in the application of this enzymatic digestion process to commercial operation. The digestion tank must be acid-proof, requiring construction of stainless or porcelain-covered steel or other corrosion-resistant material. The tank must be steamjacketed, equipped with a slow-speed stirrer, and fairly tightly covered. Unless there are workers at the plant throughout the 24 hours, fully automatic controls are required for the digestion equipment and for the sources of steam. The hazards of handling acid materials are added to those from the caustic usually employed. The protracted digestion period requires a larger investment in materials and equipment than is required in the alkali digestion process. Considerable care is necessary to avoid excessive foaming when the sodium carbonate is added to the acid mixture. These and other similar reasons probably account for the apparent lack of interest in this process by industry.

Extraction Process for Livers of Very Low Oil Content

Brocklesby and Green (ibid.) reported a method whereby the oil-soluble vitamins may be recovered from those livers from which the oil cannot be extracted directly. Salmon livers often require such special treatment. The minced livers are covered with any suitable oil, such as grayfish liver oil or pilchard oil, and heated to 212° F. (100° C.). The cooking process is continued, with stirring, for 30 to 60 minutes. The added oil penetrates the liver tissue and by its solvent action removes some of the liver oil and vitamins. The mixture may then be passed through a suitable centrifugal to remove the oil, or the oil may be drawn off after a settling period. Additional lots of oil may be stirred with the cooked liver mass in the same manner to recover still more of the vitamins. Since the cooked livers would not spoil readily, especially while they were covered by the oil layer, they could be shipped to central plant for the separation and refining of the vitamin-bearing oil. It is suggested that oils for feeding animals, for example pilchard body oil, could have their vitamin A and D content increased by being used as wash oils in the extraction of salmon livers or other suitable material. If the wash oil becomes highly enriched, it can be blended with lower potency oil to give a product that will be most efficient for stock-feeding purposes.

In some commercial operations the procedure of extracting with a solvent oil has been adopted in a somewhat modified form. The solvent oil is added to the minced livers in the digestion tank in an amount equal to 5 to 10 percent of the weight of the livers, and the operations are continued as described under the alkali-digestion section. A series of wash oils may be added to the waters from the oil separator if the vitamin content of the original liver has not been sufficiently recovered in the first oil solvent operation.

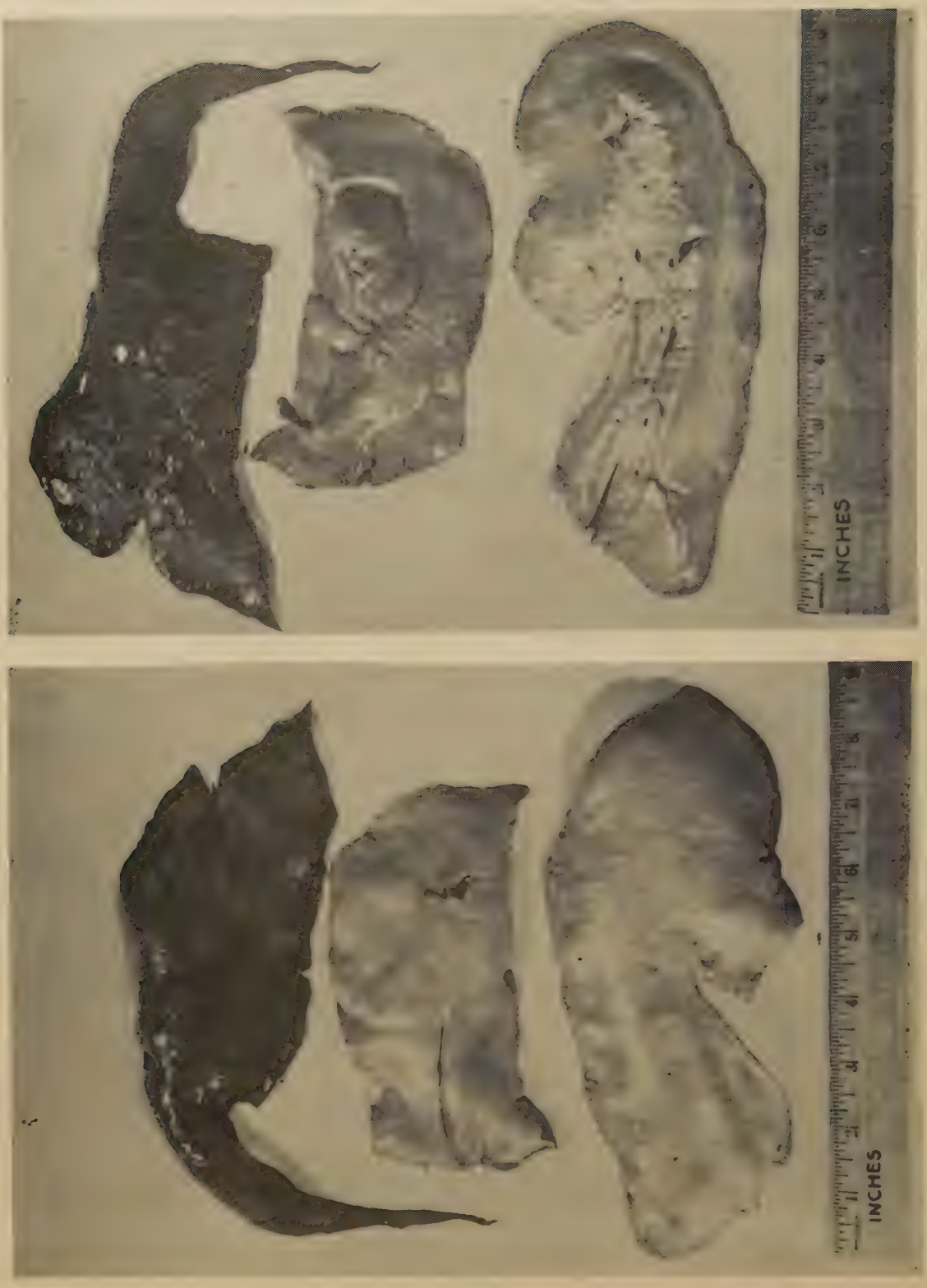

Figure 10. Upper photo, dorsal view, lower photo, ventral view of: left - rockfish (Sebastodes ruberrimus) liver, middle - lingcod (Ophiodon elongatus) liver, right - halibut (Hippoglossus hippoglossus) liver.

Acid Digestion Processes

U. S. Patent 1,833,061, issued to Jan Arent Schonheyder van Deurs (8) in 1931, describes a process for the treatment of fatty raw materials, such as animal or vegetable tissues, to recover the fat contained therein. He claims that the addition of acid to the macerated material until a pH of 1.5 is attained, with subsequent cooking and agitation, alters the surface tension of the components so that the fat may be liberated more readily.

Harrison and Hamm (9) reported a series of experiments in which they tested the efficiency of several fish liver extraction processes with grayfish (dogfish) livers. The acid digestions of frozen livers gave as good recoveries of vitamin A as did the alkali or steaming methods. Fresh livers yielded approximately the same vitamin values by the acid cook method as by the steaming process, and approximately 50 percent more than by the alkali process.

Solvent Extraction Methods

The solvent extraction methods were employed for the removal of oils from fish livers before the alkali processes were developed. Nielson was granted Patent Number 2,078,404 in 1937 covering a "Method of Extracting Liver Oil" which he claimed was far superior to solvent extraction methods previously in use. Livers, such as those from halibut, were steamed at 158-167° F. (70-80° C.) with suitable stirring for 30 to 45 minutes. The cooked livers were then drained free of the aqueous material while they were still hot and placed in containers. To protect against oxidation of the oil in the livers they were covered with a layer of paraffin, or the air in the containers was replaced by carbon dioxide gas. The livers were then cooled as rapidly as possible to minus 10° F. (-23° C.) or lower. Subsequently, the chilled livers were extracted with peroxide-free diethyl ether or a similar solvent. The extract was filtered and evaporated in vacuo. The solvent was recovered for re-use, and the liver residue was re-extracted.

Advantages claimed for the method include the uniform breaking up of the tissues and uniform coagulation, protection of the oil from oxidation by the steam, and, as a result of these factors, a much larger recovery of vitamins from the fish livers.

In all the solvent processes, the chief difficulties have been:

1. That the solvent must be free from peroxides and other impurities that have a deleterious effect on the keeping quality of the finished oil.

2. That the extracted oils have darker colors, higher viscosities and, possibly, foreign odors as a result of the rather severe conditions

(8) Jan Arent Schonheyder van Deurs, 1931. U.S. 1,833,061. Process for treating fatty raw materials.
(9) Harrison, R. W., and W. S. Hamm, 1941. Extraction of vitamin A from dogfish livers. Pacific Fisherman, 39, (9) 37-39.

under which these oils are separated from the livers.

3. That the free fatty acids, whether initially present or formed during the process, remain in the oil unless it is subsequently alkali refined.

Fish Viscera

There had been some sporadic interest in fish viscera as a source of vitamin A in the period prior to 1940. The stimulus of wartime requirements renewed this interest. Several processors have tried to handle viscera, especially from halibut and sablefish; but apparently only a few have been successful, since this material is not traded in as generally as fish livers. One Canadian processor at Prince Rupert has always purchased fish viscera. At this writing, at least three companies are believed to be processing a substantial portion of the halibut, sablefish, and lingcod viscera in the North Pacific area.

The pharmaceutical houses formerly solvent-extracted viscera as well as livers. Presumably, alkali digestion methods also have been tried out; but, from the results of laboratory experiments it appears that considerable modification would be necessary before a satisfactory vitamin recovery could be expected from such a process. Brocklesby (10) suggested that, since the alkali-peptized proteins of viscera have a greater adsorptive capacity for the oil than do those of livers, some other methods should be developed. He found that, if the viscera were cooked and pressed to remove excess moisture, solvent extraction of the vitamin oil was feasible. However, the present methods of reducing the moisture content to the required level (approximately 10 percent) are too expensive for practical application.

Usually there is a considerably lower oil content and somewhat higher moisture content in the viscera than in the liver of the same fish. If the stomachs are discarded by the fisherman, the viscera are reduced about 40 percent in volume with no appreciable loss of oil or vitamin A content. The stomachs are also very difficult to grind and digest.

Since the enzyme content of the viscera is available to begin decomposition action as soon as the fish is dead, this material deteriorates very fast unless some preservative or inhibiting action is taken. If the fisherman is to deliver the vitamin-bearing material in good condition, he should take these extra precautions.

Fish viscera usually command a somewhat lower price than the livers from the same species. At one time, for example, sablefish viscera were quoted at 35 cents a pound compared to $1.25 for sablefish livers.

EFFECT OF STATE OF LIVERS ON PROCESSING PROCEDURE

Vitamin-bearing materials may reach the processor in any of several states of preservation. Obviously, with the possibility of wide variation

(10) Brocklesby, N. H. (Editor), 1941. Chemistry and technology of marine animal oils with particular reference to those of Canada. Fish. Res. Bd. Can. Bull. 59, 222.

in processing procedures, it is difficult to discuss how all the processes can be applied to all the differing materials. The usual states or conditions of the livers and viscera will therefore be outlined and a brief statement made of the advantages and disadvantages of each generally used processing technique for each type of raw material. There is some unavoidable overlapping of this section with the section following in respect to the reasons for the types of preservation employed. The detailed discussion of spoilage in that section should be applied also to the practices mentioned here.

Fresh Livers and Viscera

The general trade practice is to use the term "fresh" to describe raw material that is not frozen or that has not had a preservative added. Thus fresh livers and viscera are encountered that have undergone varying degrees of decomposition. In processing such material, the actual degree of decomposition is of some importance. If the processor is handling high oil content-low vitamin A potency livers by the steaming method, it may be that any excessive free fatty acids developed during decomposition will be carried over into the finished oil. Odors from the decomposition products of the protein present in the livers may also be retained by the oil so that a product having undesirable characteristics is obtained.

The same decomposed livers, if processed by the alkali digestion procedure, will use up some of the added alkali to convert the free fatty acids present to soaps. These soaps then act to stabilize the oil-water-protein emulsion in the digestion stage and to adsorb some of the vitamin A contained in the livers. The emulsion may be broken to free the oil if proper equipment and technique are used; but the oil and vitamins adsorbed in the soap are not always recovered, even if wash oils are added to the water portion for subsequent oil-solvent extraction purposes. The wash oil, even after it has been enriched with the oil and vitamin A in the soap, represents a lower potency material than could have been recovered from the original liver in a fresh condition. Furthermore, the extra operation indicated may raise the cost.

Solvent-extracted vitamin oils, as previously mentioned, contain all the free fatty acids of the raw material, and only a second refining process will remove them when an amount in excess of the minimum allowable percentage is carried over into the extracted oil.

Frozen Livers and Viscera

Raw materials that are kept frozen undergo very little change in their condition. Spoilage does continue even at a very low storage temperature (-20° F., -29° C.), but the rate is so slow that, if air is excluded from the containers, no great alteration of the material takes place. If, then, the fish livers are in good condition when frozen and kept in cold storage not more than a few months, the processor receives a raw material that is practically as good as it was at the time it was frozen. The frozen livers

may then be thawed at room temperatures to permit removal from the containers. There should be no prolonged delay after the livers are thawed before processing is begun. The freezing action has broken down the tissues, and the decomposition by bacterial, enzymatic and oxidative action may proceed more readily than would be the case with fresh material.

Figure 11. Soupfin-shark (Galeorhinus zyopterus) liver, weight 5 pounds, from fish weighing approximately 50 pounds (22.7 kilograms). Color is grayish-black, with mottling pronounced. Texture is soft. Left photo is dorsal view. Note clefts at right. Right photo is ventral view. Note characteristic ridges and clefts. (Photos courtesy Laucks Laboratories, Inc.)

Figure 12. Removing livers from grayfish aboard otter trawler. (Photo courtesy Pacific Fisherman)

There are differing opinions in regard to the effect of freezing on the processing of livers. Some reports indicate that, because of the rupture of cells, the contained oil is more readily freed from frozen livers. Others indicate that any significant differences cannot be attributed solely to the effect of freezing. If, for example, the vitamin A is not present only in the oil but is also in some manner associated with the protein, rupture of the cells may or may not facilitate removal of vitamin A in processing.

One difference between frozen and fresh livers which may be significant is that thawed livers will usually produce a considerable quantity of free oil that rises to the top of the container. This may be a disadvantage for several reasons. If the livers have been allowed to thaw enough to permit the freed oil to come to the surface and then are re-frozen, the sampling of the re-frozen material by the usual core method may be in error since the freed oil will constitute a disproportionately large part of the sample. Such oil is almost invariably of lower potency than the oil remaining in the tissue. Any free oil present is more subject to mechanical loss in the process of handling, grinding, and pumping the livers to the digestion tank; and the containers must be more carefully cleaned to recover all the oil.

Frozen livers are obviously not so readily used from the standpoint of flexibility of plant operations. A sufficient supply must be thawed in advance for each day's operations. Any mechanical troubles that interfere with scheduled production may thus result in too many thawed livers at one time, or conversely, not enough at another. Ideally, the frozen reserve is of greatest advantage in a plant in which some fresh livers are received reasonably steadily. Any gluts may be frozen and later removed for processing at those seasons when either no fresh livers or small lots of fresh livers may be expected. The local fleet sailings may be used in some cases as an indication of the approximate time of return with livers. Experience and proper observation of local conditions enable the operator to make the best use of plant facilities for a steady and economical operation.

Salted Livers

The practice of salting livers to preserve them has been followed, for the most part, in fisheries in areas that do not have freezing, icing, or processing facilities near at hand. An example is the shark fishery of Lower California. Livers are salted also in South and Central America, the Caribbean area, Japan, Europe, and South Africa.

The proper technique for salting should include the following:

1. Prompt handling of fresh livers.
2. Removal of blood and slime with salt water.
3. Removal of gall bladder.
4. Cutting of liver into sections not over 2"-3" in thickness.
5. Preservation with 10 percent by weight of good quality salt.
6. Packing in containers with as little exposure to air as possible.

Livers so treated will be struck through with the salt sufficiently to preserve them for several months. Improper methods--such as the use of spoiled livers, insufficient cleaning, the use of too little salt, or the uneven distribution of salt over the livers--will result in a correspondingly poor product.

Some processors have encountered considerable difficulties in adapting their processing techniques to salted livers. Others receive the major part of their raw materials in salted form and report no serious processing difficulties. Salting dehydrates the tissues, and livers so preserved will be more difficult to grind and digest than fresh or frozen livers because of the difference in moisture content.

Brocklesby and Green (11) reported on their experiments in processing salted livers and viscera from halibut by the alkali digestion method and the pepsin modification. In the first series of tests the livers and viscera were first macerated and then intimately mixed with 10 percent of their weight of salt. In the second series the livers and viscera were salted whole. The salted materials required the use of more alkali to peptize the protein. In some cases materials that could be processed in a fresh state with 2 to 3 percent of sodium hydroxide required as much as 8 percent of alkali for digestion, and even this amount did not yield a completely liquified digest suitable for centrifuging. Such high concentrations of sodium hydroxide led to the formation of an excessive amount of soap which was difficult to remove from the oil. Similar difficulties, to a lesser degree, were encountered when the pepsin digestion process was employed.

Formalin-Preserved Livers

In the same study by Brocklesby and Green, tests were also made in which the preservative used was formalin in the amount of 0.25 percent by weight. With ground material, the proteins that were dissolved in the liquid coagulated and caused the entire mass to solidify. With whole livers and viscera, the outer layer became case-hardened, this occurrence suggesting that the preserving action may not be uniform throughout the material.

Some Pacific Coast processors have observed similar conditions in formalin-preserved (and in salt-preserved) shark livers. However, in each case the fault may have been with the technique employed by the person treating the livers.

Brocklesby and Green reported that no decomposition of the formalin-preserved materials took place over a two-week storage period at room temperature. Digestion of the livers with the alkali or pepsin process was satisfactorily done. In fact these workers stated that the digestion was somewhat more easily carried out than was possible with the control livers. Excessive amounts (2.5 to 5 percent) of formalin resulted in the formation of small, hard lumps of material that resisted digestion, but

(11) Brocklesby, H. N. and K. Green, 1938. The Preservation of Halibut Livers and Intestines. Fish. Res. Bd. Can. Prog. Rept., Bull. 36, 7-9.

such concentrations were not needed for preservation under the conditions of these tests.

Other Preservatives

Mention was made before of the use of aquacide (U.S. Pat. No. 2,107,245) as a preservative for codfish livers in the maritime provinces. In that particular case the flotation process described was developed by the manufacturer of the preservative. The manufacturer advertises that anyone using this product will be advised of the proper methods to be used for processing livers so preserved.

One of the satisfactory preservatives for thoroughly ground materials is a solution made up of nine parts soda ash, one part sodium nitrate, and ten parts water by volume. This solution is used in the proportion of 5 percent of the weight of the ground livers (12). Since the soda ash is a mild alkali similar to that frequently used in the digestion process, no particular difficulties should arise in the processing of livers so preserved.

FACTORS AFFECTING THE QUALITY OF THE OIL PRODUCED

The factors to be considered here will be grouped under the following headings:

1. Freshness of Raw Materials.
2. Process Used.
3. Storage Conditions of Livers and Oil.

Freshness of Raw Materials

The importance of the freshness of fish livers at the time they are processed has been recognized for many years. The Norwegian Government has drawn up rather rigid regulations that must be complied with if the producer wishes to market his product as medicinal grade cod liver oil. These regulations specify that the livers must be fresh and free from gall bladders. Time and temperature ranges for processing the livers are given, as well as directions for storage of the finished oil. Medium grades may be sold as animal and poultry feeding oils, and the poorest or cod oil grade is no more than an industrial oil like whale or seal oil. The cod liver oil industry of Newfoundland is even more closely regulated. Icelandic cod liver oil manufacturers are under the direct supervision of governmental agencies to insure that the quality of the product is maintained. In the Pharmacopoeia of the United States, Twelfth Edition, cod liver oil is defined as being made from fresh livers, and halibut liver oil from fresh, or suitably preserved, livers.

The criterion for classifying livers according to freshness is somewhat a matter of opinion. In areas such as the North Atlantic, temperatures do not become unduly high during much of the fishing season. Off the coast of

(12) Guide to Commercial Shark Fishing in the Caribbean Area. U.S. Fish and Wildlife Service, Fishery Leaflet 135, 33, 1945.

Southern California, temperatures are sufficiently high practically the year around to cause rapid spoilage of fish livers.

Ice is often employed to retard the decomposition of the protein and oil which is caused by bacteria and enzymes. However, the degree of retardation is not as great as with freezing; and, if the livers are preserved with ice alone for more than a few days, they will become badly decomposed.

As soon as the fish die, the enzymatic action begins to break down the body tissues. This is especially true of the digestive tract where the enzymes that act on food taken into the system will also decompose the organs themselves after death. For this reason, viscera are especially difficult to keep for even a very few days without some preservation procedure.

The products of the bacterial and enzymatic action, such as certain sulfur-containing compounds, amines, etc., may be taken up by the oil; and their objectionable odors may carry over into the finished oil, rendering it unsalable or of lesser value. Livers exposed to the air may be subject to oxidation of the oil; and a third form of deterioration--rancidity--may then affect the quality of the oil.

To minimize these three types of spoilage and to keep the livers and viscera in the best possible condition, the following precautions should be taken. The livers and viscera should be placed in separate containers as soon as possible after the fish are caught and butchered. The containers should be in a clean, sanitary condition and free from remnants of former lots that might infect the new lot with bacteria. The containers should be tight to prevent leakage, and they should be filled as close to the top as possible to reduce the volume of air present. The lids should seal the containers tightly. On the fishing boat, containers of the livers and viscera should be packed in ice just as carefully as the fish which are to be used for food.

A square, five-gallon can with 7-inch, triple-seal, friction lid affords good protection to the contents; and, if it is properly taken care of, may be re-used a number of times. For larger lots of materials, the 55-gallon steel drum with removable head, sealing gasket, and a positive mechanical clamping device for securing the head in the drum also is satisfactory from the standpoint of ease in cleaning, freedom from leakage, and prevention of ready access to air. There is some disadvantage to these larger drums in that their handling on the dock, in cold storage, or at the plant involves the use of either mechanical lifts or considerable hard labor. Generally the 5-gallon cans are used aboard the vessel. After they are landed, they are thoroughly chilled; and the contents are then dumped into the larger drums before being moved into refrigerated storage.

When the livers and viscera are removed from the hold of the vessel, many buyers sort and grade the materials at once. If there are decomposed livers mixed with those in better condition, sorting may enable the buyer to segregate like materials; or, if several species of different vitamin A

Figure 13. Grading Grayfish (Squalus suckleyi) livers. (Photo courtesy Laucks Laboratories, Inc.)

potency ranges are present and identifiable, the actual value of the purchase may be more accurately estimated. Any extraneous materials such as water, ice, free salt, rocks, shells, tramp iron, etc., are also removed, where possible, at this time.

An identifying lot mark or code number should be fastened to, or placed on, each container to insure proper grouping of lots for processing and to enable the processor to keep an accurate check on the cost of his raw materials and the value of their recovered products. If the purchases are to be stored, they should be packaged in accordance with the instructions previously given and frozen as rapidly as possible. If the materials are used immediately, the containers should be thoroughly cleaned and aired as soon as they are emptied.

Process Used

The method of treating the fish livers and viscera has a bearing on the quality of the vitamin oil that is extracted. Several of the methods were previously mentioned, and the characteristic limitations and advantages of each of the more important ones will be discussed here.

Steaming

Steaming--the process of rendering the oil from the livers by the action of steam and stirring--is perhaps the simplest method available from the standpoint of cost and equipment. Livers may be handled in large volume; and, if they are fresh, the resulting oil

should be of good quality. If the livers are thoroughly processed, the enzymes present will be destroyed so that no further deterioration may be expected from this source in the finished oil. However, most of the free fatty acids present in the raw livers may be expected to appear in the oil. If very stale livers are used, the resulting oil may have to be further refined by alkali treatment before it can be marketed.

Solvent Extraction

This procedure is being more widely used at present than in the past, especially in the extraction of vegetable oils from such materials as soya beans, cottonseed, etc. It is possible that, from the experimental work on such products, the disadvantages previously encountered in solvent extraction of fish livers and viscera may be at least partly overcome. These disadvantages include, so far as quality of the oil is concerned, the effect of impure solvents, of prolonged heating or high temperatures, and of contact with metal surfaces that may catalize the alteration or discoloration of the oil.

Some solvents such as ether, etc., often contain peroxides, which accelerate the oxidation of the oil during the extraction and the subsequent removal of the solvent by distillation. The specific solvent used should be tested for its effect on the color and vitamin content of the finished oil.

Prolonged heating or high temperatures in the cooking, extraction and distilling stages may increase the discoloration of the oil by causing accelerated oxidative action and actual deterioration or alteration of the pigments in the oil. In solvent extraction, the free fatty acids present in the livers are carried over into the finished oil.

Alkali refining to remove these free fatty acids usually results in some bleaching of the oil, but the red discoloration due to overheating is not readily removed.

Alkali Digestion

The most widely used of the vitamin oil recovery methods is the alkali digestion process in some one of numerous modifications. The combination of thorough cooking, agitation, and peptization serves to inactivate the enzymes and reduce the free fatty acid content of the finished oil. If the amount of alkali is so adjusted to the requirements of the particular batch of material that no great excess is supplied, soap formation should not be excessive enough to cause bothersome emulsions or to carry off a significant amount of adsorbed vitamin A in the water phase.

There has been some research on the resistance of alkali-processed vitamin oils to oxidation. If oils are to be stored for prolonged periods, oxidation becomes a very important cause of loss of vitamin potency in storage. However, the stability of the oil is also definitely linked with the state or condition of the livers before they are processed, and so no one reason may be definitely assigned for instability. Some brief mention of

stability is made in another section of this report for those who are specifically interested in the subject. In view of the rather widespread adoption of alkali processing at present there seem to be no serious objections that outweigh the advantages this process offers.

Storage and Shipment of Oils

In all the oil extraction processes employed, constant vigilance must be maintained to recover a maximum amount of the vitamin content of the liver or viscera in a form as high in quality as is consistent with the methods and equipment at the disposal of the processor. The precautions that should be taken to protect the oil from the time it is recovered until it is actually consumed are equally important. Among the factors that will merit our consideration are:

1. Type of container,
2. Storage temperature,
3. Sunlight and atmosphere,
4. Moisture or foreign matter.

Type of Container

Some companies prepare the vitamin oil for shipment soon after the final processing. Various shipping containers may be used. Low potency oils for the animal and poultry trade or for concentrators are pumped directly from the storage tanks in the plant into the tank car or boat tank. Usually no special precautions are required other than the routine inspection of the empty tank by the railroad or the certifying agent for cleanliness and freedom from objectionable odors or foreign matter. The tank car should, however, be filled to the specified maximum content to minimize air space.

If vitamin oils are shipped in drums of 5, 15, 30, or 55-gallon size, the containers should be clean, dry, and free from rust. The headspace in the drum should be kept to a minimum. An inert gas, such as carbon dioxide or nitrogen, should be introduced to displace as much of the air as possible before the drum is sealed. Usually the bungs are protected by a seal of sheet metal or wire and lead to prevent them from loosening in transit and to make any attempted tampering readily apparent.

Some imported cod liver oils have been marketed in drums that are tin-coated inside to minimize the action of the metal surface on the vitamin or the oil, but producers here have not followed this practice. Perhaps some of the newer types of enamels would serve as well as tin to keep the metal surface free from rust prior to the filling of the container. However, tests would be required to determine whether such coatings might have deleterious effects that would not become apparent until later.

Temperature

Oils stored in either tanks or drums should be kept cool. Changes of a chemical nature, such as oxidation, proceed at a much faster rate as the

temperature of the oil increases. Another effect may be noted in oils stored for a time in a cool place: the stearins, the solid fat portion of the oil, will be precipitated from the liquid portion. If a representative sample is to be taken for analysis from a container in which this precipitation has taken place, it may be necessary to stir the contents of the tank or drum thoroughly. In order to blend various lots of these stored oils it may even be advisable to warm the oils sufficiently to allow the stearins to return to the liquid state either before or during the blending operation.

Light and Atmosphere

In some plants, fish liver oils have to be stored in tanks for a period of a few days. For example, a low-potency oil may be stored in tanks until a carload has been processed; or various oils from the same species may be grouped by potency ranges in a series of tanks. As orders for vitamin oils come in, the tank containing oil of the desired vitamin A content is thoroughly blended and the required amount of oil barreled out. In such instances, the tank should be constructed so that there is no direct or indirect sunlight reaching the stored oil. Ideally, an inert gas should replace the air over the oil, but this is not always feasible. Sunlight and air accelerate undesirable changes in the oil and, in turn, may destroy the vitamin A as well.

Moisture and Foreign Matter

If an oil has been properly prepared, it should contain less than 0.3 percent of moisture, no suspended protein or nitrogenous material, and not over 0.03 percent of sediment other than stearin or waxes. Moisture in stored oil is objectionable since it usually contains some dissolved or suspended nitrogenous matter that will decompose and form the objectionable and evil-smelling products already mentioned. If the moisture content exceeds 0.3 percent, bacteria can multiply; and they may cause deterioration of the oil also.

Tanks that are allowed to remain empty for a time after the oil has been removed should be thoroughly cleaned before being filled with a second lot of oil. The film of oil on the sides and bottom of the tank will have been exposed in a thin layer to oxidation; and, unless the peroxides so built up in this oil are previously removed, they will begin at once to destroy the vitamin A in any subsequent oil placed in the tank.

FACTORS FOR CONSIDERATION IN CONTEMPLATED BUSINESS VENTURE

The success or failure of a new business venture will depend to a considerable degree on the thoroughness with which the organizer investigates the factors which affect the contemplated operations. Obviously these factors will vary widely with locality, market conditions, scope of operations, etc. Those discussed here are typical of the factors that should be considered by anyone interested in a fish liver processing business.

Processing Equipment

Many types of equipment can be used for the preparation of vitamin oils. In the selection of the equipment for a particular plant some of the items to be considered are: (1) kind and volume of material, (2) process contemplated, (3) availability and relative cost of power and heat from the various sources such as electricity, steam, water power, internal combustion engines, etc., (4) amount of mechanization and automatic control, (5) cost and availability of labor.

Many of these factors may be difficult to evaluate accurately in advance for the localities being considered. Even estimates made on the spot at the time the contemplated business venture is being initiated will be subject to considerable error. Therefore, only the factors for which a fairly close approximation is possible are enlarged upon here.

Steaming Method

Let us assume the simplest and most inexpensive conditions, within reason, and set up the approximate equipment requirements for a given capacity of production. The steaming process for low potency shark livers will fall into this category.

The livers should be ground in either a conventional meat grinder or in a hammer mill. A vertical hammer mill capable of disintegrating approximately two tons of liver per hour will cost from $1,200 to $1,800. Smaller sizes would be somewhat less expensive.

The ground livers should be transported to the cooking tanks by means of a gear pump to minimize churning of the material. A suitable pump to handle the output of the above-mentioned grinder costs $150 to $300. A trap basin should be installed in the pipe-line between the outlet from the grinder and the pump to minimize the amount of rock and tramp iron introduced into the gear pump. A shear pin of sufficiently small diameter is often advisable to protect the pump in case such solid materials do travel that far. Valves on the liver pipe-line should be self-cleaning and non-clogging.

Cooking tanks may be fabricated of wood or iron, depending on the desires of the processor and the availability of material. As an example of the relative cost, in the Seattle area, for tanks of approximately the same dimensions and 1,000 gallons capacity, those made of iron cost approximately $100, and those of wood cost $65. If heating is to be direct steam, the only cost, other than piping, valves, etc., might be for an automatic steam controller at $50 - $100 per tank to regulate the temperature of the cook at the desired temperature. If cooking is accomplished by indirect steam heating, there will be the added cost of the pipe coils. Agitation may be by a portable electric mixer, a fixed side-entrance stirrer, or a stirrer fixed on top of the tank and driven by a chain or belt activated by suitable shafting and gears. Portable stirrers are available in various

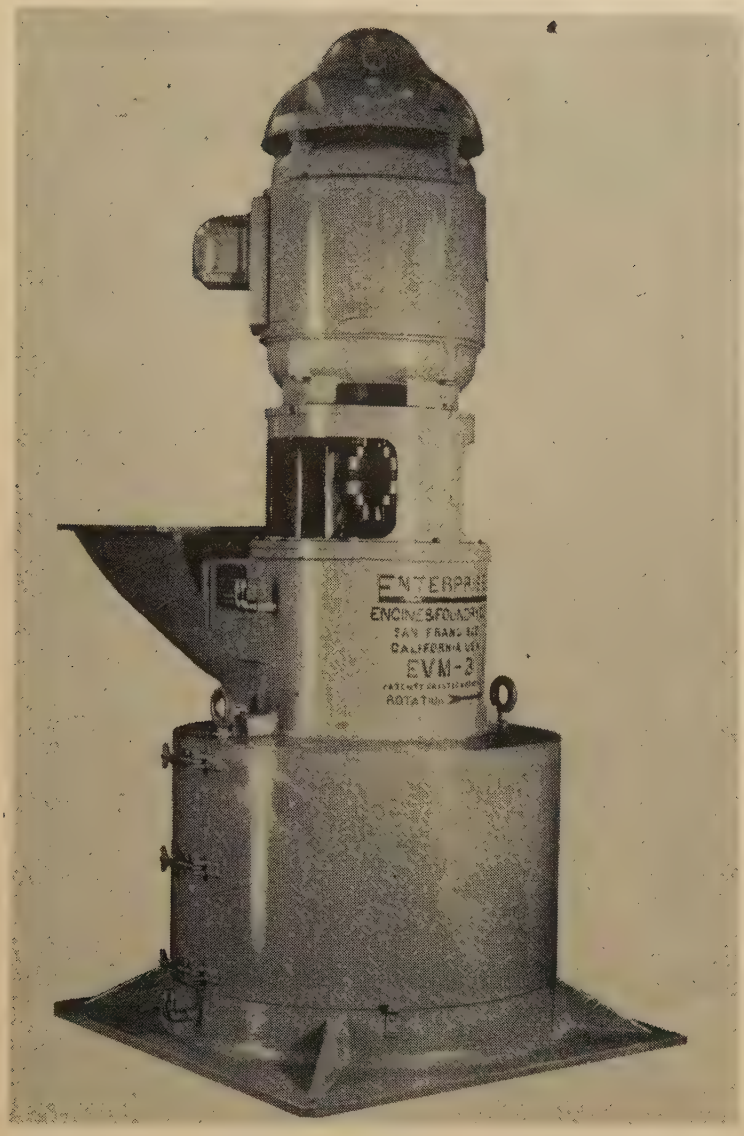

Figure 14. Vertical Mill for grinding livers. (Photo courtesy Enterprise Engine and Foundry Company.)

horsepower ratings and motor speeds. One brand of stirrer having a 1½-horsepower motor and operating at 1,750 revolutions per minute costs approximately $185. The same brand with a ½-horsepower motor costs approximately $110.

Several variations in the application of centrifugals for the separation of fish liver oils are in use by the processors. If the steaming process is used on a small scale, it is possible to get fairly high oil recovery by allowing the material in the cooker tank to settle until the upper or oil layer separates before it is drawn off to be processed in the oil purifier or centrifuge. An imperforate basket centrifuge may also be used to separate the liquid constituents from the solids prior to the final purification of the oil. For larger operations, the entire contents of the tank are first passed through the sludger centrifuge to remove the wet oil from the solids; and then the wet oil is finished in the purifier centrifuge.

There are two principal manufacturers of the centrifugals now being used in the fish liver oil industry. Each company manufactures the three-phase, or sludger-type, machine designed to accomplish the continuous preliminary separation of the cooked or digested liver material into (1) an emulsion of oil, water, and fine solids and (2) a sludge of water and coarse solids. The larger centrifuge of this type has an approximate capacity of 1,500 to 3,000 gallons of liquor per hour. The actual performance will be determined by the character of the material to be separated, and there may be some variation in capacity from one lot of material to another. The sludger of this capacity range costs $6,000 to $8,000 depending on whether stainless steel construction or standard equipment is ordered.

The second machine—the oil purifier or polisher—is designed to recover the oil in a marketable form from the oil-water-fine solids emulsion of the

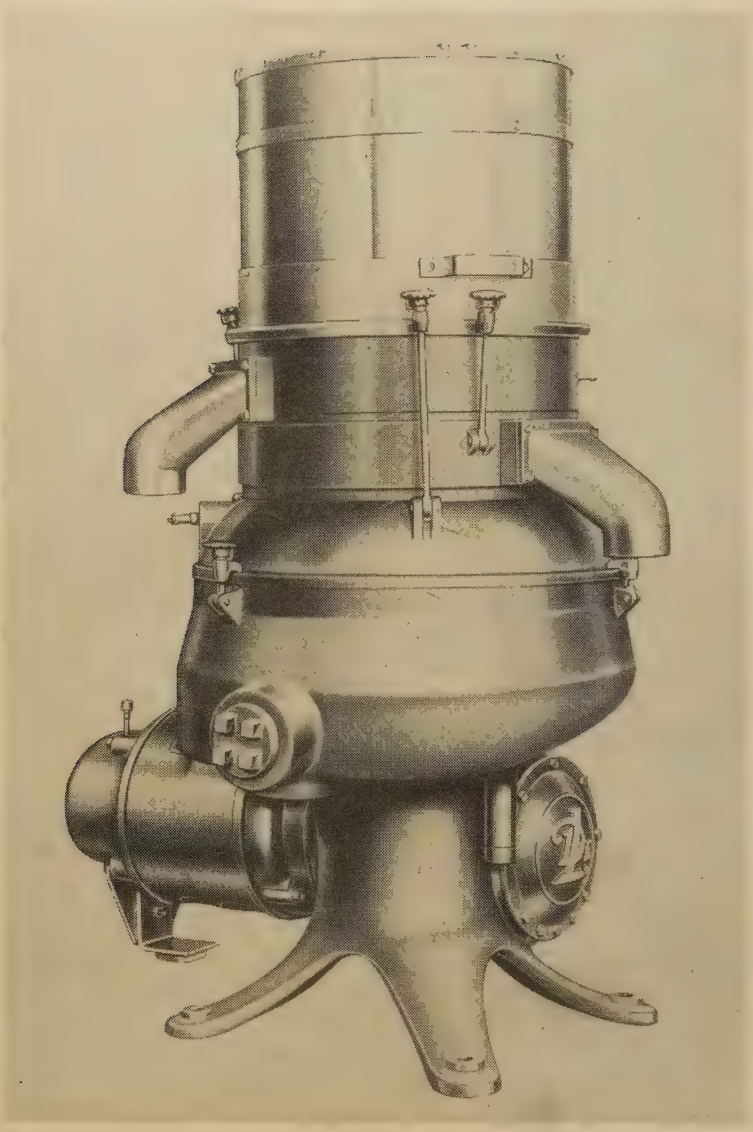

Figure 15. Three-phase, or sludger-type, fish liver oil separator. (Photo courtesy De Laval Separator Company.)

sludger-type centrifuge. These purifier machines are available in several sizes. The approximate costs for the usual industrial models are $1,800, $2,400, and $3,500.

Centrifuges may require a rather large supply of hot water for satisfactory performance, especially if the sludger machine is used. Therefore, there should be provision for an adequate supply of water at 180° - 190° F. (82°-88° C.).

The boiler capacity required for liver processing varies considerably with the process and plant equipment, but a rough estimate would be 10 boiler horsepower per 1,000 gallons of cooker capacity. Boiler costs are dependent on type and local rates. A 10-horsepower boiler suitable for a fish liver plant should cost approximately $500.

Plants processing large amounts of livers will need a gear pump to move the oil from the centrifuge to the tanks used for storage or for blending and mixing. A portable stirrer or other agitator is required for these tanks, and steam coils are usually desirable to warm the oil sufficiently to facilitate mixing in case it has become viscous or partly solid at lower temperatures.

Alkali Digestion Method

Equipment for the alkali digestion method of processing is somewhat different and more elaborate. The grinder, liver pump, and cooker tanks are similar except that, since the livers are usually diluted with an approximately equal quantity of water, twice as many cooker tanks are required for the same capacity as with the steaming method. Agitator requirements are

Figure 16. Fish liver oil centrifuge. (Photo courtesy The Sharples Corporation.)

practically the same for the cooker tanks, except that, if portable stirrers are used, more units should be available so that processing is not delayed in case digestions require longer to complete than had been planned. If the wash oil technique is to be employed, several additional tanks and stirrers will be needed to accommodate the water from the digestions. Usually a pump is used to transfer the water discharge from the centrifuge to the wash-oil tanks. By means of a second pump, the contents of the washing tanks are returned to the centrifuge. If it is so desired, suitable piping arrangements may be made to use one pump for a series of tanks for either cooking or washing. The wash-oil tanks should have some provision for maintaining the temperature of the liquor at about 180° F. This may be done by either direct or indirect heating with steam.

The alkali process requires a close control over the pH of the liver mass during the digestion period. Several companies make equipment which measure pH. A small, portable, industrial model costing approximately $150 may be used; or the more elaborate, automatic recording model is available for approximately $750.

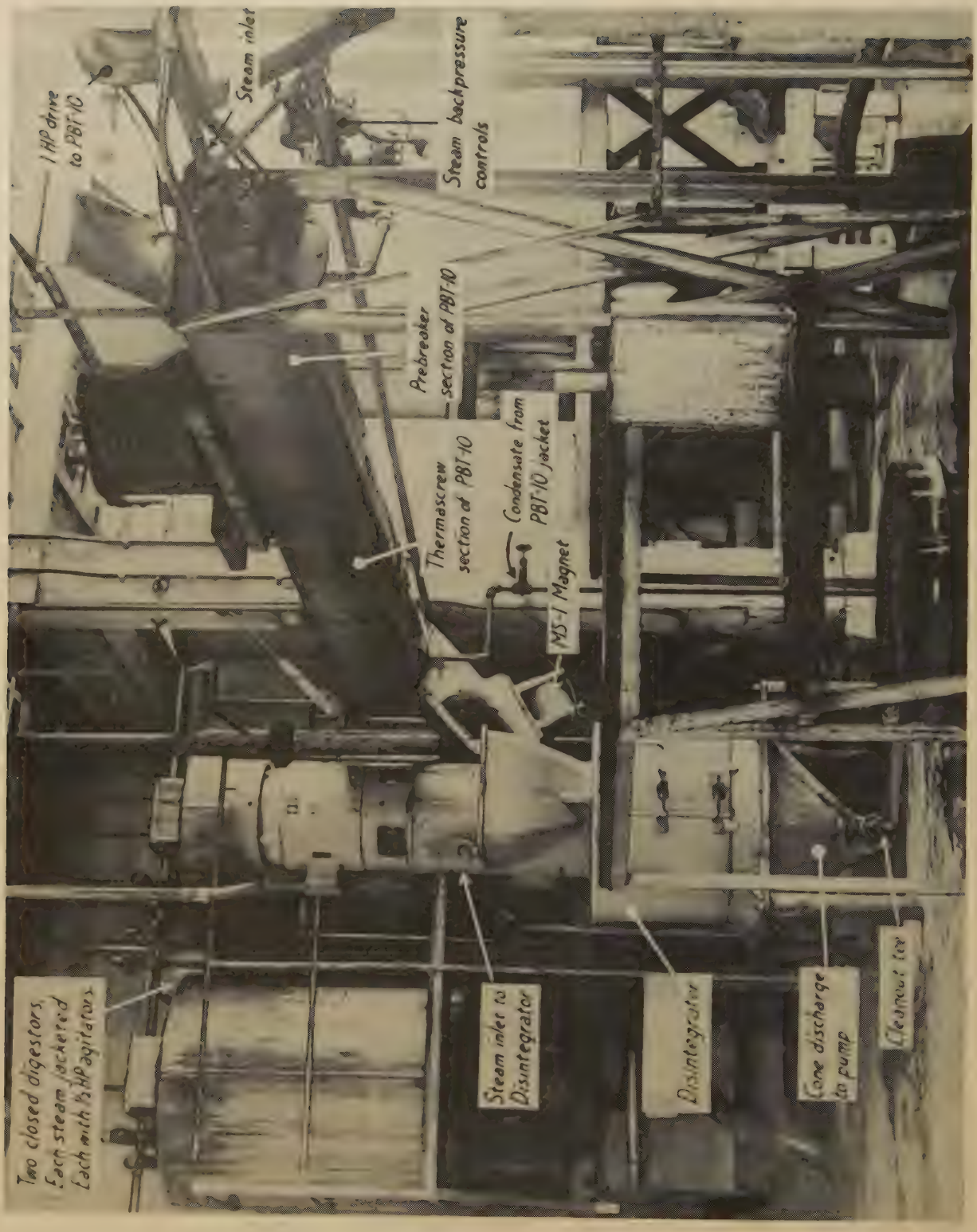
1 HP drive to PBT-10
Steam inlet
Steam backpressure controls
Prebreaker section of PBT-10
Thermoscrew section of PBT-10
Condensate from PBT-10 jacket
MS-1 Magnet
Two closed digestors. Each steam jacketed Each with ½ HP agitators
Steam inlet to Disintegrator
Disintegrator
Cone discharge to pump

Figure 17. Liver disintegrator installed. (Photo courtesy Process Machinery Company.)

With the alkali process, both the sludger and the oil purifier centrifuges are necessary unless only small amounts of materials are to be handled. A surge tank equipped with stirring and steam heating facilities should be available to receive the skim from the sludger. Any treatment to facilitate the breaking of the emulsion in the skim liquor may be accomplished in this tank before the liquor is passed to the oil purifier.

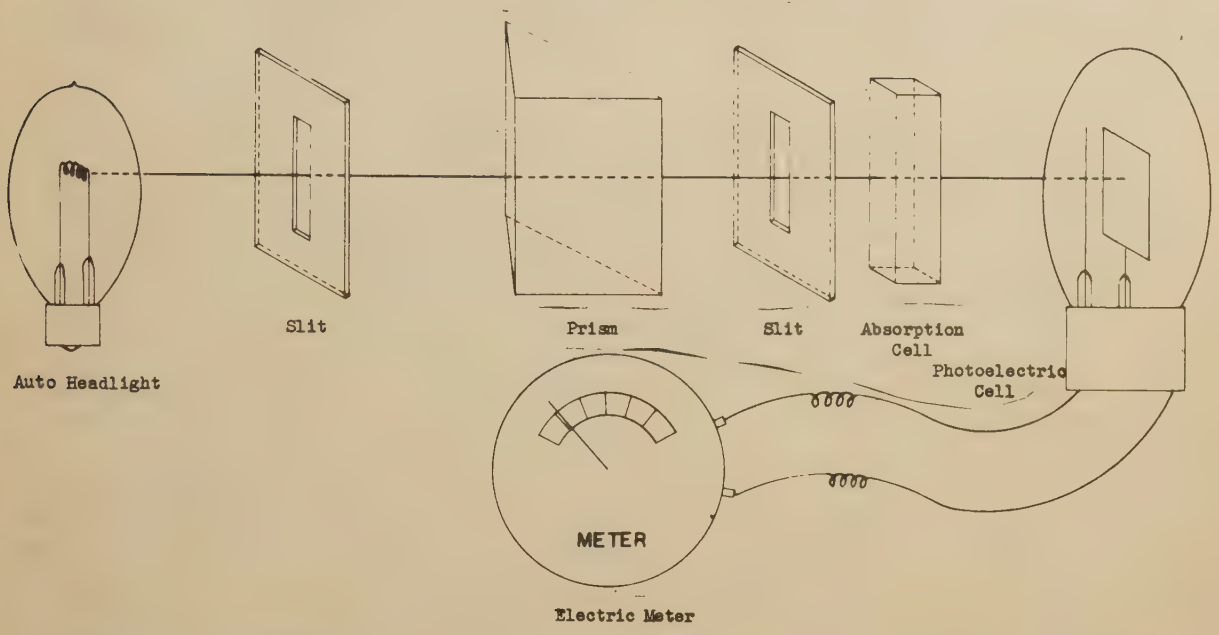

Figure 18. Schematic drawing of operating principles of the photoelectric spectrophotometer.

When livers that are expected to yield higher potency oils are processed, the oils are usually collected in separate drums or tanks in accordance with the anticipated potency and the species from which the livers are derived. The wash oils are kept similarly segregated. Sufficient storage facilities must be provided for these lots of oils until they are ready for shipment.

Equipment for Estimation of Vitamin A

The most widely accepted physical method for the measurement of the vitamin A content of oils is by means of the spectrophotometer. There are several manufacturers of this type of equipment. During the war, the members of the vitamin oil industry in the U. S. standardized on the Beckman instruments made by National Technical Laboratories. These spectrophotometers cost from $750 to $1,200. The services of a technically trained man or a chemist are required to insure the proper use of this equipment; and, since it is rather delicate, proper laboratory facilities should be supplied if it is to be of the most value to the plant. Several other spectrophotometers, ranging in price from $200 to $400, are available, such as the Coleman Universal, the Lumitron abridged spectrophotometer, and the Photelometer.

For the measurement of vitamin A by the Carr-Price color reaction, instruments are available over an even wider price range. The least expensive, the LaMotte testing kit, costs approximately $35. Several of the other manufacturers mentioned above have models suitable for use with this chemical method at prices of $100 to $400. The Evelyn Colorimeter is another instrument in this price range. By means of an adapter developed at the Seattle Technological Laboratory of the Fish and Wildlife Service, the Beckman spectrophotometer may now be used for the Carr-Price reaction also.

Sources of Raw Materials

If there is already an active fishery at the location under consideration, the volume of livers and viscera available from the fish landed can be readily approximated. Fishermen usually have some general ideas about the types of fish that are taken on their gear but are not being purchased and are therefore not brought to port. The abundance of such bothersome species may not always be properly estimated by the fishermen since they may be biased unduly by a relatively small number of valueless fish appearing in the catch. For example, to the early halibut fisherman, grayfish were a pest, since they were not salable then and each one on the hook cut down the potential haul of halibut per skate of gear. In such cases the fisherman may overestimate the abundance of these nuisance species. Unless accurate biological studies have been made of a fishery, the level of sustained production that may be expected cannot be predicted. For example, the halibut fishery of the North Pacific is believed to be sufficiently well regulated as a result of years of study that in the future a definite annual poundage can be reasonably expected. For such a fishery, the livers and viscera available can, therefore, be rather accurately estimated. On the other hand the abundance, life cycle, etc., of albacore tuna are not known well enough to give even a general idea as to the probable catch in future years.

Cost and Volume of Raw Materials

Even where the natural resource of suitable vitamin-bearing species is adequate, the estimation of what quantity of raw material will be available for purchase and what its cost will be is very difficult and involves the consideration of such factors as the following:

1. Current local market for livers and viscera and for food fish.
2. Current market price for vitamin oil.
3. Current supply of vitamin oil moving to satisfy markets.

A few cases from actual experiences on the Pacific Coast will illustrate how these factors may influence the production and cost of vitamin-bearing materials. The otter-trawl fishermen based in Seattle can choose whether they will fish for the food market or seek grayfish for the liver market.

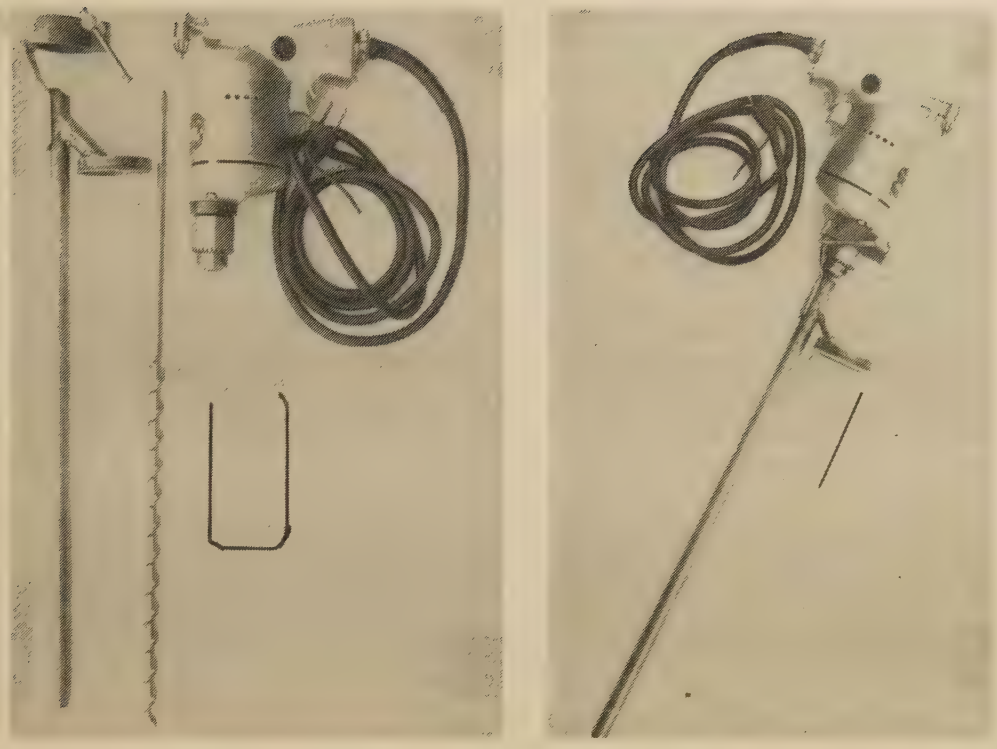

Figure 19. At left, liver-sampling device disassembled. At right, liver-sampling device assembled.

During periods of low prices or large supplies of food fish, the fishermen may find it advantageous to make one or more trips for livers. The wartime ceiling prices on food fish, on occasion, enabled fishermen to earn a much higher income from fish livers which were eagerly sought by the buyers at prices not directly under ceiling limitations. Then, too, at certain seasons weather conditions or the migrations of certain species of fish render a trip for market fish unprofitable; but the continuing demand for vitamin A is an inducement to gamble on the prospect of a large haul of soupfin shark or grayfish. In fact, many boats, which formerly would have been tied up during the winter or during the off-season for food fish, now are operated during almost the entire year, in great part as a result of the growth of the fish liver industry.

If, then, the volume of fish livers marketed in a given area is small, it does not necessarily indicate that potential supplies are limited. In some instances the fisherman has in mind an arbitrary price per pound of livers below which he will not exert himself to fish for the commodity. For example, at one time Alaskan fishermen refused to bring in grayfish livers for less than 15 cents per pound. The processors contended the livers were worth less than that price because the oil and vitamin A content was low in that area. Vitamin-bearing raw material from the New

England trawl fishery is largely dumped at sea because the boat owners and fishermen cannot agree on the sharing of the expenses that would be incurred and the revenue that would be received if the material were saved and landed.

In some areas there are the additional complications from contracts already existing between the fishermen and processor or buyer. For example, processors have, in the past, contracted at a fixed price for all the livers produced by a given group of fishermen, such as those in the halibut fleet. Companies frequently have an interest in boats and may, by agreement, divert any livers to desired channels. Recently the organization of cooperatives has been an important development. As mentioned previously, groups of Canadian fishermen combined into a cooperative to process, in their own plant, fish livers and viscera. As another example of the factors affecting the availability of raw materials, in Seattle the halibut fleet rejected the bids of processors for livers and viscera in 1940, and for several years the halibut fleet has had its entire landings of vitamin-bearing materials custom-processed into marketable oils by a Seattle processor at a fixed fee per pound of liver plus a sales commission based on the gross value of the oils. This arrangement definitely limits the supply of such livers that will be offered on the open market to what is available from halibut fishermen who do not join the organization or to halibut livers taken incidental to another fishery, such as salmon trolling.

In those cases where competition for fish livers was keen, the established buyers were formerly in a better position to bargain, by benefit of their past experience. With present methods of sales based on an assay of a representative sample of the lot of livers, much of the guess work has been taken out of liver purchases. The assay shows the theoretical maximum oil and vitamin A content present. The efficiency of the prospective purchaser's extraction methods, the need for the vitamin A, and the market price for the particular potency range of the oil contained in the lot of livers become the determining factors in a decision regarding the procurement of the proffered stocks of livers.

From any and all sources possible, then, complete information should be gathered on the local conditions, present and probable future. The Federal and State fishery organizations may have data showing the species of fish taken, the percentages of liver and viscera present, the potency ranges, and the oil contents. Tables 3, 4, and 5 in the appendix summarize available information of this type. Ideally, the investigator should have such data from a large number of individual specimens, segregated according to sex, maturity, length, and season. The significance of these segregations lies in the fact that the value of livers and viscera may vary widely with differences in one or all of these categories. For example, studies by Sanford (13) indicated that, for specimens of the same sex and similar maturity from a given locality, the vitamin A content of grayfish livers

(13) Sanford, F. B. and G. I. Jones. Liquid Gold. International Fisherman and Allied Worker 6, No. 4, 5, 1946.

definitely increases with the length of the fish. If the liver of a male fish 36 inches in length would bring $0.67, a liver (from the same lot) from a second male fish 39 inches in length would be worth $1.17. Soupfin-shark livers are usually segregated according to sex, since the livers of the males have a considerably higher value than do the livers of the females. Rapson and Schwartz (14) in South Africa studied the variations in oil content and potency of stonebass livers over a 16-month catch cycle. They reported that potency was at a minimum in August, increasing to a maximum in November. Oil content was variable in a reverse manner, being highest in May and lowest in October to December. The net effect on the vitamin A content was to increase the value of the livers at the potency maximum since the oil content varied less widely. There was some slight variation in the size of the livers which approximately paralleled the variation in oil content.

Plant Location and Site

The location in which a fish liver processing plant is to be placed is governed by two general considerations: (1) restrictions commensurate with sound economics of operation, and (2) legal restrictions, if such are then in force, or may subsequently be invoked.

In the first group, the obvious matters should require little discussion here. The sources of raw materials should be as close at hand as possible to lessen handling, storage, and preservation costs and to insure prompt processing of fresh livers. If water frontage is available so that fishermen may bring their livers directly to the plant, handling is lessened. In some cases it may then be necessary for the processor to be in a position to furnish the fishermen with such goods and services as:

1. Ice, salt, or other preservatives.
2. Minor boat repair parts and supplies.
3. Gear replacement parts and supplies.
4. Food, clothing, fuel, and oil.
5. Potable water.
6. Water or other facilities for cleaning the boat, etc.
7. Limited or seasonal housing.
8. Entertainment.

Perhaps this list of items seems unduly detailed; but, if the fisherman can make only one stop for the various essentials of his trade, he will be better satisfied to do business with a company furnishing such services.

If the volume of production is to be significant, the plant site should be chosen with a view of accessibility to utilities and supplies such as water, power, fuel, transportation, communications, and cold storage facilities. The exact requirements of these items will vary with the materials to be handled, the processing methods used, and local conditions.

(14) Rapson, W. S. and H. M. Schwartz, 1944. South African Fish Products, the Stonebass. J. Soc. Chem. Ind. 63, 18-21.

Most of the processes would require a reliable and adequate steam supply, which is, in turn, related to good sources of water and fuel. Power for the operation of the equipment may be supplied by electricity, steam, or internal combustion engines. Some Canadian canneries have utilized water power also. Adequate transportation is important to get raw materials and supplies to the plant and to move the finished products to market. Communications can be essential, especially if emergencies of any kind arise.

Cold storage facilities serve multiple purposes. If livers are received in a fresh state in quantities too large for immediate processing, they may be held frozen with little deterioration. Small amounts of livers or viscera from the various species may be stored separately until lots of convenient size are accumulated. At certain seasons this diversity of species may be quite a problem. If the potency or oil content of the various livers is very different, a pooled lot may not be as profitable to the processor as the individual species would be if handled separately. In emergencies, which will always arise because of mechanical breakdowns, power failures, etc., the liver receipts may be stored until the plant is ready to operate again.

Disposal of Processing Wastes

The problem of waste disposal should not be overlooked in planning a processing plant. Careful consideration of the local conditions and the equipment available plus proper judgment in lay-out can obviate many difficulties. Most cities are now zoned, usually into residential, business or commercial, manufacturing, and industrial zones. Fish liver processing is, in a sense, a manufacturing process; but, owing to the concomitant odors and waste products, it is generally classified as an industrial operation.

It may be possible to carry on processing of some materials without the evolution of any characteristic odors, but most plants do give off these odors. For example, a fish cannery will always have the aroma, pleasant or otherwise, of cooking fish. Lumber mills, pulp mills, etc., likewise produce characteristic odors. It is suggested, therefore, that local people be assured that every reasonable precaution will be taken to control and render inocuous the processing odors and to dispose of wastes in a satisfactory manner. This frank and open promise must then be carried to consummation. Plants now in operation in congested areas have installed fume scrubbers, chemical-treated towers, air washers, and combustion chambers for the elimination of odors.

A sewer connection or some system for satisfactory disposal of waste products is essential. Municipalities and states are becoming more pollution conscious; and, in many instances an approved disposal system must be included in the plans before a building permit will be issued. If the local sewage system utilizes some procedure that may be incompatible with the wastes from a plant, a treatment may be necessary before this material can be discharged into the sewer.

Another alternative to the pre-treatment of the wastes by the company is the consummation of an agreement for the municipality to take over the task. Several cities have made contracts of this type. Usually a survey is made to determine the volume and character of the material to be run into the sewer by the individual plant. If this survey indicates that this material is compatible with the industrial wastes from other sources and with the normal sewage of the city, the charges for treatment may be agreed upon by the interested parties. For example, the ordinance for the city of New Brunswick, N. J., states that all wastes must be treated at the municipal plant. The charges for this treatment are based on the volume of flow, the content of suspended solids, and the chlorine demand for the particular industrial wastes of a plant. The schedule of rates for these three basic categories are: $22.00 per million gallons, $5.00 per ton of sludge, and $5.00 per 100-pound chlorine demand.

Several advantages have been observed from the treatment of domestic and industrial sewage in one processing plant. As a rule, the total cost of such an operation would be less than for two separate sets of equipment. The efficiency of the treatment may be more easily and frequently checked. Industrial concerns which are required to pay their share of the expense for sewage treatment usually attempt to keep their wastes to a minimum. This desire to cut down sewage-disposal costs would serve several purposes: the burden on the municipal treatment equipment would be less severe, the waste materials recovered by the industrial concern could be a source of additional revenue, and the efforts on the part of the plant management to find uses for the wastes recovered would be increased.

This may be illustrated by an example of a slaughterhouse in which excessive amounts of solids and fats were being washed into the sewer. An investigation resulted in the installation of a more efficient screen to recover practically all of the solid materials. A grease trap assisted in the removal of the fatty substances. These materials were then routed to the by-products plant where they actually returned a profit over and above the cost of the equipment installed to separate them from the industrial wastes going to the sewer.

In more isolated localities, raw wastes have often been dumped into a nearby stream or lake. This practice should be discouraged. Treatment systems based on suitable modifications of known techniques can condition the wastes so that they can be disposed of without causing objectionable pollution.

Some techniques involve the precipitation of the solids by centrifugation or by chemicals such as aluminum sulfate. In other treatment methods most of the solids are allowed to settle out in a series of retention lagoons, and then oxygen is supplied by direct aeration or by the addition of sodium nitrate, and the solids are subjected to aerobic bacterial decomposition. When the treatment is complete, the waste may then be drained off to a stream with a minimum of deleterious effects.

Sanborn (15) studied the lethal effects of various concentrations of sodium hydroxide, calcium hydroxide, sodium carbonate, sodium nitrate, aluminum sulfate, and ferrous sulfate on three species of fish. His conclusions were that the discharge, under prevailing conditions and with adequate dilution of these chemicals, which are commonly used in the treatment of cannery wastes, is not toxic to fish.

Aid in the selection of the most suitable method of waste disposal for a particular installation can usually be obtained from the sanitary engineers of the State health department or from the State university or agricultural college.

Disposal of Fish Carcasses

In the State of California it is unlawful to bring shark livers to shore unless they are accompanied by the corresponding carcasses, each with head, fins and evidence of sex intact and attached. The regulation has not always been strictly enforced. It does not apply to shipments of livers originating in other states or in foreign countries. If such regulations are enacted elsewhere, the liver processor may be obligated either to branch out into general fish meal and oil production or to have a separate operator nearby who will take the carcasses from the fisherman. Then, too, states may have legislation, such as Washington has, that no fish fit for human food taken within the waters under the jurisdiction of the state may be used for animal feeding. These possibilities are mentioned here merely as a reminder to inquire into the existing legal restrictions in any tentative plant site before a final decision is made.

Availability of Experienced Personnel

For a fish liver processing plant the problem of key personnel merits consideration. The duties have been arbitrarily divided into three categories: (1) buyer, (2) processor, and (3) chemist. In a small plant one man could conceivably handle more than one set of duties, but for purposes of discussion this division will be used here.

The Fish Liver Buyer

The primary function of the fish liver buyer is to handle transactions with the fishermen. This position involves more than merely receiving the livers, making the payment to the fisherman, and passing the livers on to the processing department. The buyer, to be successful, should know the fishermen personally, keep in close contact with them, understand their point of view, and maintain amicable but business-like relations for the plant. In some instances it may be necessary for him to be conversant with methods of handling and preparing for shipment the fish and other products the fisherman brings to the plant. It is common practice, in some localities, to sell the fish livers to the company buying the fish. To insure a supply of livers a processor may, therefore, have to get into the fresh and frozen fish business unless suitable arrangements can be made with

(15) Sanborn, N. H., 1946. Lethal Effect of Chemicals on Fresh Fish. Food Packer 26, No. 8, 40-41.

another local company to handle the fish.

The livers themselves require attention in sorting, identification, and proper storage. If livers are purchased outright, some system of evaluation for payment will be required. This has, in the past, consisted of "blind buying" based on the values previously recovered as vitamin A from similar livers. Depth of color, mottling, size, or markings on the livers have been used as indices of value. These methods are effective only if an experienced person does the judging, and even then the results are subject to great error. For example, experienced gained with livers in one locality often does not apply in the identification and evaluation of livers from an entirely different locality.

The best current method available for evaluation involves the collection of a representative sample of the lot of livers, the extraction of the oil from the sample, and the measurement of the vitamin A content of the oil. Since this process requires the services of a chemist or a technically trained person, details of these duties will be included under that section. In some cases a consulting laboratory may be available to do the

Figure 20. The fish liver sampler in operation.

sampling and analysis on a fee basis. In any case the buyer should be informed on these subjects himself, in order to understand and interpret the reports from the laboratory.

Since the fish buyer is in close contact with the fishermen, he is the logical man to supervise or advise on the purchase and distribution of the items of food, clothing, supplies, gear, etc., mentioned in the previous section, if such service is maintained. Considerable good will can be built up for the company if facilities for the maintenance and repair of gear and boats are properly managed. If these services are conducted on a business basis, the fishermen lose less time ashore; and the operation may even pay tangible dividends as well.

The Processor

Inside the plant, the task of converting the fish livers or viscera into vitamin A oils is the duty of the processor. Obviously these responsibilities will vary with the type and volume of livers being processed in the particular plant. However, in any case, the processor must be able to conduct or supervise the extraction processes being employed. He should know the characteristics of fish livers, have a good working knowledge of the chemistry involved in the reactions taking place, and be thoroughly familiar with the operation, maintenance, and repair of the mechanical equipment in the plant. This knowledge may be acquired by experience in similar plants or by a combination of formal education and practical experience. Since the vitamin oil industry is relatively new and the various modifications of the several standard methods mentioned are closely held secrets of the present operators, the supply of men with all these qualifications is strictly limited. A new company must either find such a man or train and develop a processor to fill its needs. For the latter contingency a chemical engineer would be suggested as having a suitable background.

The Control and Research Chemist

As was mentioned in the discussion of the duties of the liver buyer, the processing plant may have to sample and assay livers. Even if this is not required for the actual purchases, the chemist will be interested in checking periodically the oil content, potency, salt content, etc., of the livers to be processed. As each lot of livers is being processed the potency of the final oil (and of each wash oil where such are used) must be measured by the chemist. By a comparison of the plant recoveries of vitamin A with the theoretical or assay results, a constant check may be kept on plant efficiency. Oils may need to be analyzed for free fatty acid content, moisture, and unsaponifiable residue for purposes of plant control or for conformance with sales specifications.

When the new company is beginning operations, the chemist is available to consult with the head of the processing department in working out the most satisfactory technique of processing the livers and in solving the problems that will arise from time to time with materials as variable

as fish livers. An aggressive organization, in addition to following the quality and quantity of production with control tests in the laboratory, will be continually utilizing its chemist in research. The results of such research may lead to improvements in processing technique, to a better use of the waste products, or to entirely new products, uses, or activities.

Some plants do toll processing. Livers owned by some other company or individual are sent to the plant for extraction of the liver oil. This oil may be sold by the owner of the livers as he sees fit. The processing plant charges a fee for this service. Usually the toll rates are based on the quantity and kind of livers treated. In such cases the chemist acts to protect the processor's interests by weighing and sampling the lot of livers, checking the processing in the plant, and analyzing the oil recovered. He is then able to issue to the owners of the livers a certification showing the amount of livers, assayed value, oil recovered, and vitamin A content of this oil. If an outside laboratory is acting as referee on the premises, these functions are performed by the referee's chemist; but the processor's chemist should verify the data.

One other source of fish livers is the fish dealer who purchases small lots of livers from the fishermen and then re-sells the pooled lots to a processor. Usually the dealer performs this function as middleman for a fee of approximately 10 percent of the value of the livers. Livers so handled will be checked by the chemist as in the cases mentioned above. He may also be of service to the dealer by instructing him in the segregation and handling of the livers so that the vitamin A content may be properly protected and most efficiently recovered by the processor.

DISTRIBUTION OF FINISHED OIL

Vitamin oils, as they come from the processing plant, may be ready for marketing or they may require additional treatment. The two chief types of such oils, stock-feeding oils and pharmaceutical oils, obviously go into different markets and therefore will be subjected to different treatments.

Feeding Oils

Oils of the low potency class may be sold, as they are, to mixers of animal and poultry feeds. Some producers of sardine and herring body oils blend sufficient additional vitamin A oils and synthetic vitamin D with these body oils to produce the several potency levels used in the feeding trade. Some standard feeding oil blends contain the following amounts of U.S.P. units of vitamins A and D per gram of oil:

1. 400 D - 1000 A
2. 400 D - 2000 A
3. 400 D - 3000 A
4. 800 D - 2000 A
5. 800 D - 4000 A
6. 85 D - 400 A

Cod liver oils with added vitamins A and D are offered as 400 D - 2000 A, and 800 D - 3000 A. These blends are shipped in steel drums or in tank cars to the feed-mixing centers or to dealers or large-scale feeders. Each drum or tank car is tested and then labeled with the minimum vitamin A potency content expressed in U. S. P. units per gram and the minimum vitamin D content in A. O. A. C. chick units, if for poultry feed, or in U. S. P. units of vitamin D if for four-footed animals.

A considerable portion of the production of low potency oil goes into the preparation of vitamin concentrates. For example, carloads of grayfish liver oil from the Seattle or Vancouver area are purchased by the companies engaged in concentrating vitamin oils. The details of the concentration processes currently in use are discussed later in this section.

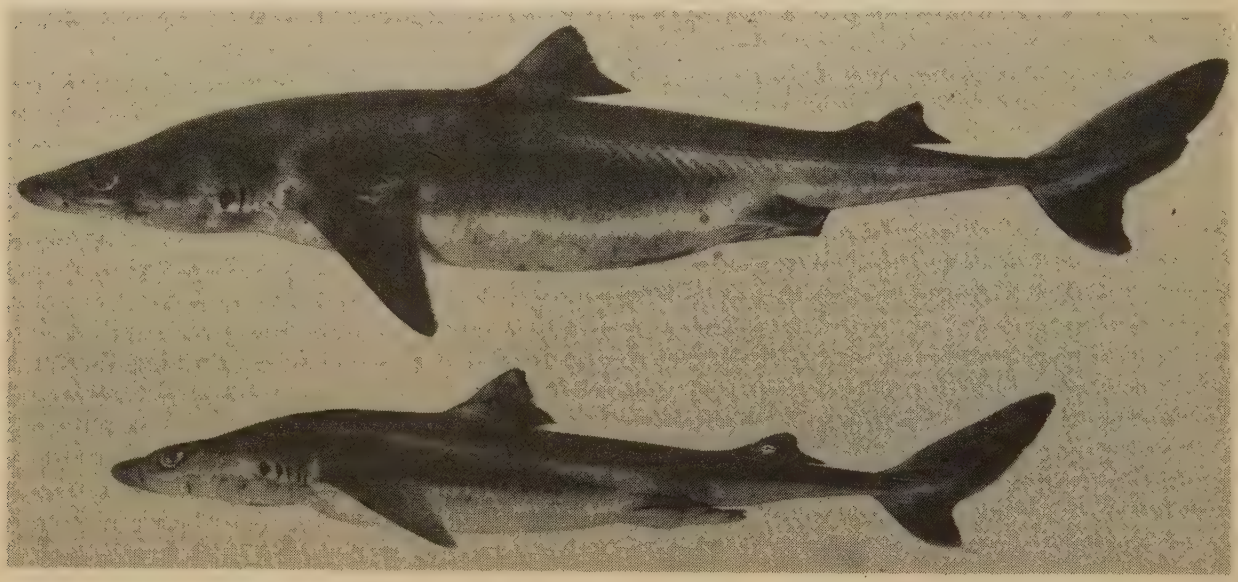

Figure 21. The grayfish (dogfish), (Squalus suckleyi). Upper, female; lower, male.

Vitamin A Oils For Human Use

Vitamin oils, such as halibut, sablefish, lingcod, soupfin-shark, and cod liver oils, are purchased by many pharmaceutical and proprietary medicine houses. In some instances an oil otherwise satisfactory has a free fatty acid content in excess of that desired by the trade. This oil may be subjected to an alkali refining process which lowers the free fatty acid content to the desired level. Such an extra operation increases the cost of the vitamin oil by reason of both the processing expense and the loss of some of the vitamin A content of the original oil.

Once a satisfactory oil has been obtained, several different marketing forms may be utilized by the pharmaceutical house. The oil may be packaged into various sizes of bottles. Cod liver oil has been sold in this manner for years. The oil may be partially concentrated and sold as a higher potency bottled oil.

Vitamin oils in bottles may be subject to deterioration from several causes. As the package leaves the manufacturer's plant, the bottle is almost full so that little air space is left. The bottle is usually placed in an opaque wrapper or carton; or, if it is for unwrapped display, brown glass may be used. These precautions of the manufacturer give reasonable assurance that the vitamin potency will not deteriorate while the product is stored in the warehouse or in the drug store. Ewe (16) examined unopened bottles of cod liver oil that had been stored under such conditions for two and two-thirds to four years and reported practically no loss of potency. Some liver oils are not so stable, largely because the processing required to extract them also removes or alters the natural antioxidants originally present in varying amounts in most liver oils. When these antioxidants no longer protect the oil, destruction of the vitamin content may proceed more rapidly. Liver oils processed from stale raw materials are more liable to undergo this accelerated decomposition.

Bailey (17) reported his observations of the effects of conditions usually encountered in the home on vitamin A potency. He stored vitamin oils for a period of six months in full bottles and bottles one-fourth filled, in clear glass and brown glass, at room temperature and at 30° F., and in light and in dark. The variations in the potencies of the oils subjected to these diverse conditions led him to the conclusion that, of the factors investigated, oxidation caused most of the destruction of the vitamin A. Capsules stored under these same conditions showed little loss of the vitamin A content of the oil. He recommended that vitamin A oils be stored in a cool, dark place and that the bottle have a minimum of air space over the oil.

The oil either as received or with additional vitamin and mineral supplements, may be processed into capsules as liver oil capsules or multiple vitamin capsules containing vitamins A, B, D, G, etc. One process for capsulation is described below in detail.

Since there is a limit to the size of capsule that can be comfortably swallowed, high potency oils or concentrates are generally employed for encapsulation, especially when the capsule contains a blend of the oil with other vitamins. The maximum standard drug specification for capsule size is usually five minims. Potencies offered in capsules may be grouped into several classes. The average person who purchases vitamin capsules from the drug store gets either a 5,000-unit vitamin A capsule or the so-called high potency, 25,000-unit capsule. These are offered to meet the daily needs of the normal individual for vitamin A. In cases of serious vitamin A deficiency, physicians sometimes prescribe capsules containing 30,000 to 100,000 units of vitamin A each. Such large doses should not be taken without medical supervision.

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(16) Ewe, G. E., 1934. Stability of Cod Liver Oil under Commercial Distribution Conditions. J. Am. Pharm. Assoc. 22, 1085-1086.

(17) Bailey, B. E., 1943. Stability during Household Storage of Vitamin A. Fish. Res. Bd. Can. Prog. Rept., Bull. 54, 15-17.

In addition to the use of vitamin A in pharmaceutical preparations, a second source of supply for human use is in fortified foods. The oleomargarine industry has annually purchased substantial amounts of high-potency vitamin A oils and concentrates to be incorporated into its product. Before 1945, the usual fortification level had been at approximately 5,000 U. S. P. units per pound of oleomargarine. After rather extensive research, the industry has increased the vitamin A content of the margarine to 12,000 - 15,000 U. S. P. units of vitamin A per pound.

Capsulation of Vitamin Oils

A widely used method for dispensing vitamin A for human use is in the form of capsules. Robert P. Sherer (18) developed the Rotary Die Process in 1933, and the machines based on this method have largely superseded all other capsulating processes.

In the United States, this rotary die process machine has been perfected to such a point that very large capacity, exact fill, and low unit-cost operations are possible. A widely diversified list of materials are now custom-processed into capsule form. Manufacturers and dealers in vitamin oils send the vitamin A oil, and any other ingredients in case a multiple-vitamin capsule is desired, to the owner of the encapsulating machine.

A mixture of gelatin, glycerine, and water is prepared and placed in the reservoir of the encapsulating machine. Two continuous ribbons of this gelatin emerge from openings in the reservoir, are passed over a pair of large forming rolls, through a mineral oil bath, and between the two die rolls. An injection wedge, situated between the converging ribbons at the die rolls, admits through tiny holes the exact amount of material desired per capsule. This material is under pressure sufficient to expand the gelatin ribbons against the sides of the die pockets. As the rolls converge, the two sides of the capsule are sealed together by heat, and the completed capsule is severed from the perforated ribbons of gelatin. A stream of cold air cools the finished capsules as they roll toward the collecting tray. The mineral oil coating on the capsules is removed by a dry-cleaning process before the product is packaged and shipped to the trade. A charge of approximately 10 cents per 100 capsules is made for this encapsulating service.

Concentration of Vitamin A by Molecular Distillation

Molecular distillation has been employed for many years as a laboratory method for the purification of various materials. The equipment available did not lend itself well to the organic materials such as are present in fish liver oils until suitable high-vacuum condensation and fractionation pumps were developed. After long and careful experimentation, the cost of vitamin concentration by this method has recently been brought down to a competitive level. An excellent description of the

(18) Anonymous, 1943. Tubes, Capsules and Enclosures. Canadian Chemistry and Process Industries 27, No. 5, 248-249.

Figure 22. Emptying grayfish from the cod end of an otter trawl. (Photo courtesy Pacific Fisherman)

present procedures used in commercial molecular distillation has been published by Oliver (19). The principal features will be brought out here to illustrate this method of vitamin A concentration.

If the pressure exerted on a gas in an enclosed space is reduced to approximately one micron, the molecules of the gas no longer interfere, by collision, with the molecules of the vaporizing substance. At this point no further lowering of the boiling point is possible. However, so long as the vaporized molecules are removed from the space, by such means as a pump, the evaporation of the substance continues at a uniform rate. Any substance can be vaporized at some rate, given a sufficiently high temperature and very low pressures. If a substance that would otherwise be damaged by the high temperature is exposed to such a temperature for only a very short time it may be possible to molecularly distill the substance without damage. One condition necessary to facilitate this process is the prompt and continuous removal of the vaporized molecules from the confined space.

This is accomplished in the modern horizontal, centrifugal-type, molecular still. The still consists of a dome enclosing the rotor, condensers, heaters, feed, vacuum, and discharge connections. By proper selection of disc size and type and speed of rotation, any exposure time desired may be made use of in distillation. After the proper vacuum and temperature are attained in the still, the liquid is fed to the center of the spinning disc. As the film moves out to the collector gutter around the rim, vaporization takes place. The condensing surfaces nearby immediately cool the vapor to liquid; and, as this condensate forms it is continuously drawn from the chamber. Any liquor not vaporized as it passes across the disc face is skimmed off through a nozzle projecting into the collector gutter.

In practice, a series of such stills is employed to treat the fish liver oil at successively higher temperatures. The products distilled off are, in the order recovered: (1) any gases contained in the oil; (2) the protein and rancidity odors; (3) the free fatty acids, sterols, vitamin D, glyceride ethers and esters, the natural preservatives including the tocopherols (vitamin E) and their esters; (4) vitamin A and its esters; and (5) the residue of glyceride fat.

At present the vitamin D content of the third fraction cannot be recovered from the other materials at a cost to compete with synthetic vitamin D. However, vitamin E is recovered by a series of fractional distillations. The vitamin A is recovered as a concentrate ready for use. Oil residues from the original distillation and from the series of fractionations to recover the vitamin E are sold for food or industrial purposes.

Similar stills are being built with a throughput capacity of from 500 to 1,000 pounds per hour. The cost for power, water, etc. is said to be well within the requirements of commercial operating limits.

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(19) Oliver, T. R., 1944. Molecular Distillation, a New Path to Separation of Chemicals. Chem. Met. Eng. 51, 100-104.

Concentration of Vitamin A by Saponification

Vitamin A has been concentrated from fish liver oils by the saponification processes for many years. Saponification is, essentially, the splitting of the tri-glycerides of the oil into glycerol and fatty acids or derivatives of fatty acids such as soaps. Some of the common methods for the accomplishment of the saponification involve the use of acids, alkalis, enzymes, or synthetic organic catalysts. Those constituents of the oil which are not directly affected by the saponification are classed as unsaponifiable matter. The vitamin A of the original oil is concentrated in this unsaponifiable matter when the oil has been, in effect, removed by the saponification. Then, if, the unsaponifiable matter is removed with a solvent and purified further, a concentrate of vitamin A is obtained.

The patent literature lists many processes for the concentration of fish liver oils by saponification. Reagents and techniques for the saponification, physical and chemical methods for separation of the unsaponifiable matter, and degrees of concentration are all described.

Most companies prepare their vitamin A concentrates by saponification processes. One factor of importance in concentration by the saponification process is the unsaponifiable matter content of the oil to be used. If, for example, a liver oil contained 20 percent unsaponifiable matter, the maximum theoretical concentration that could be effected by saponification would be five times. Some shark liver oils have a rather high content of unsaponifiable matter; and if they are of low potency -- 8,000 to 10,000 U. S. P. units of vitamin A -- they could not be expected to yield a concentrate containing more than approximately 50,000 units of vitamin A. Concentrates are usually considered to contain 200,000 U. S. P. units or more of vitamin A per gram.

VITAMIN OIL SPECIFICATIONS, PRICES, ETC.

Present U. S. P. Standards

The United States Pharmacopoeia XII lists standards and tests for the identity, quality, and purity of materials considered suitable for pharmaceutical uses. The vitamin oils listed by species in the Pharmacopoeia include halibut liver oil, cod liver oil, and non-destearinated cod liver oil. Other vitamin oils listed include oleovitamin A, oleovitamin A and D, concentrated oleovitamin A and D, and synthetic oleovitamin D.

Halibut liver oil is described as the fixed oil prepared from the fresh or suitably preserved livers of Hippoglossus hippoglossus Linne. The vitamin A content must be not less than 60,000 U. S. P. units per gram and the vitamin D content not less than 600 U. S. P. units per gram. The oil is a yellow to brownish-yellow color and has a characteristic, slightly fishy, but not a rancid odor, and a fishy taste. The oil must have the following characteristics also; as determined by the prescribed testing methods:

1. Insoluble in water, slightly soluble in alcohol, and freely soluble in ether, chloroform, carbon disulphide, and ethyl acetate.

2. Specific gravity at 25° C., between 0.920 and 0.930.

3. Free fatty acids, not more than 1 cc. of tenth-normal sodium hydroxide is required for neutralization of 2 grams of the oil.

4. Unsaponifiable matter, not less than 7 percent nor more than 13.5 percent.

5. Saponification value, not less than 160 and not more than 180.

6. Iodine value, not less than 125 and not more than 155.

In recent years, halibut liver oils have been prepared with a content of vitamin A in excess of 100,000 U. S. P. units per gram. These high potency oils often contain up to 23 percent of unsaponifiable matter, as compared with the maximum permissible content of 13.5 percent specified in the U. S. P. XII. This indicates that a change in the specification should be considered.

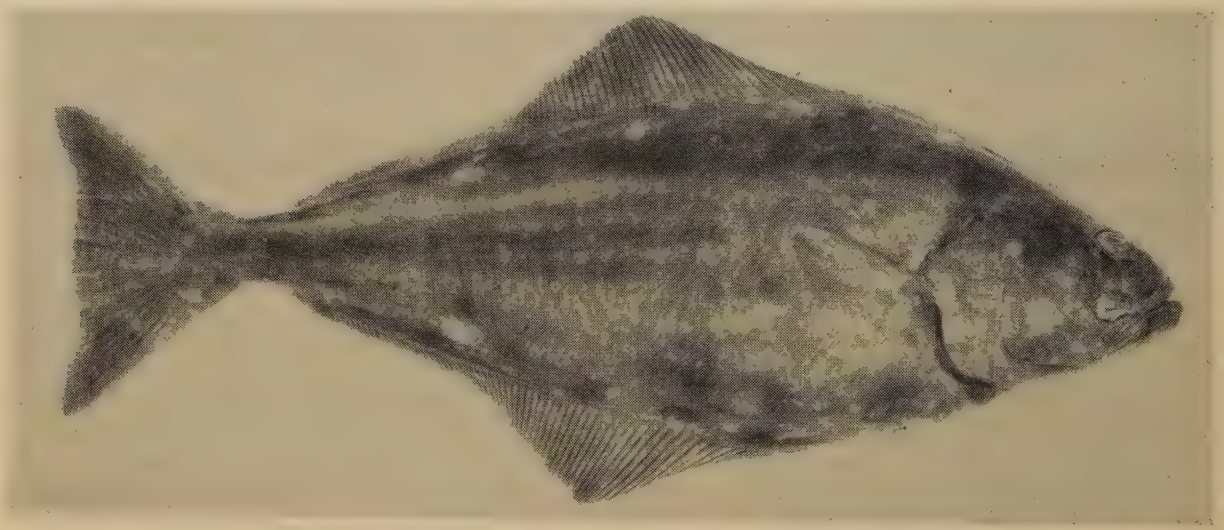

Figure 23. The Pacific Halibut, (Hippoglossus hippoglossus).

The U. S. Pharmacopoeia XII states that halibut liver oil may be identified by shaking together a solution of one drop of oil in one cubic centimeter of chloroform and one drop of sulphuric acid. A blue color, changing to violet, dark green, and brown, in that order, indicates that the material is halibut liver oil. This test is not necessarily specific for halibut liver oil, and it is believed that most higher potency vitamin A oils will give such a response.

Cod liver oil is obtained from fresh livers of Gadus morrhua Linne and other species of the family Gadidae. The potency is not less than 850 U. S. P. units of vitamin A per gram, and not less than 85 U. S. P. units of vitamin D per gram. Specifications for taste, odor, free fatty acids, and solubility are the same as for halibut liver oil. Other specifications for destearinated cod liver oil, as determined by the prescribed testing methods, are:

1. Specific gravity at 25° C., not less than 0.918 and not more than 0.927.

2. Unsaponifiable matter, not more than 1.3 percent.

3. Saponification value, not less than 180 and not more than 192.

4. Iodine value, not less than 145 and not more than 180.

5. Oil must remain clear and no stearin shall be deposited after oil has been subjected to the temperature of melting ice for three hours.

Non-destearinated cod liver oil differs chiefly in that none of the stearin occurring in the oil has been removed by the cold clearing process. Not over 0.5 percent by volume of water and liver tissue may be present in the oil, and the iodine value shall be not less than 128 and not more than 180. Other specifications are as listed for cod liver oil.

Oleovitamin A is described as either fish liver oil, fish liver oil diluted with an edible vegetable oil, or a solution of vitamin A concentrate in fish liver oil or in an edible vegetable oil. In all cases the vitamin A shall be of natural (animal) origin. Each gram of oil shall contain not less than 50,000 and not more than 65,000 U. S. P. units of vitamin A, and not more than 1,000 U. S. P. units of vitamin D. Taste, odor, and free fatty acid content are as previously described.

Oleovitamin A and D may be made up of the same combinations as oleovitamin A except that the concentrates of D also added may be from either natural or synthetic sources. The potency per gram of oil shall not be less than 850 nor more than 1,100 U. S. P. units of vitamin A, and not less than 85 nor more than 110 U. S. P. units of vitamin D.

Concentrated oleovitamin A and D differs only in that the potency per gram of oil must be not less than 50,000 and not more than 65,000 U. S. P. units of vitamin A, and not less than 10,000 and not more than 13,000 U. S. P. units of vitamin D.

Synthetic oleovitamin D may be a solution in an edible vegetable oil of either activated 7-dehydro-cholesterol (D_3) or activated ergosterol (D_2). This oil must contain not less than 10,000 U. S. P. units of vitamin

D per gram, and it must be labeled as to whether the vitamin content is D_2 or D_3. The oil solution is a clear, colorless to light-yellow liquid; is almost odorless; and has a bland taste.

War Food Administration Sales Specifications

The other vitamin oils not specifically identified by the U. S. Pharmacopoeia are sold on a basis similar to that of these U. S. P. vitamin oils. For example, during the period that the War Food Administration was buying vitamin oils for lend-lease and other governmental uses, its requirements of information to be included in the contracts for such oils were as follows:--the weight of the oil, its estimated vitamin A potency (in U. S. P. units per gram to the nearest 100 units), the price per million units based on the estimated potency level (subject to an adjustment of 1 mill per 1,000 U. S. P. units for each thousand units per gram that the estimated potency differs from the actual potency as determined by the referee analyst), the species from which derived, the method of concentration if the oil is a concentrate, and the kind and size of the containers.

The specifications of oils submitted had to show the following:

1. Source - prepared from vitamin bearing fish or marine animal material by any method with or without substitution of any edible oil in whole or part for the fish oil vehicle.

2. Color -- free from added color.

3. Odor and taste -- may have a fishy but not rancid odor or taste.

4. Impurities -- shall contain not more than 0.5 percent water by volume and not more than 0.03 percent (by dry weight) of precipitate or sediment other than stearin or waxes. Any precipitate or sediment, if present, shall be free from nitrogenous matter.

5. Freedom from excess acidity -- not more than one percent of free fatty acids (calculated as oleic acid).

6. Determination of vitamin A content of oils - vitamin A content shall be determined spectrophotometrically, subject to confirmation by biological assay. The spectrophotometric assay on the whole oil dissolved in ethanol or isopropanol will consist of measurements of the extinction coefficient ($E\ \frac{1\%}{1\ cm.}$) at the following wave lengths: 300 millimicrons, 328 millimicrons, and 350 millimicrons. The ratio of the value of $E\ \frac{1\%}{1\ cm.}$ 300 millimicrons to the value of $E\ \frac{1\%}{1\ cm.}$ 328 millimicrons shall not be more than 0.73 and the ratio of the value of $E\ \frac{1\%}{1\ cm.}$ 350 millimicrons to the value of

$E \frac{1\%}{1\ cm.}$ 328 millimicrons shall not be more than 0.65. The potency of the oil will be calculated by multiplying the value of $E \frac{1\%}{1\ cm.}$ 328 millimicrons by the conversion factor 2,000.

From each lot tendered, seven samples of three ounces each shall be drawn by designated representatives, and vitamin A assays shall be made on these official samples when submitted to two of the recognized vitamin A testing laboratories. If the results of the two laboratories are in agreement within five percent (based on the highest potency), the average of these two values shall determine the potency of the oil on this contract. If the results are not in agreement within five percent (based on the highest potency), official samples shall be submitted to two additional recognized testing laboratories; and, of the four assays, the average of the two in closest agreement shall be used in determining the potency.

7. Chemical analyses, where indicated, shall be in accordance with the provisions of the U. S. Pharmacopoeia XII where applicable.

8. Packaging - Vitamin A oils shall be packed and delivered in new, air-tight, standard metal containers not less than 18 gauge in weight for drums of 30 to 55 gallons or 22 gauge for containers of less than 30 gallons and 5 gallons or more. Head space shall be filled with inert gas, preferably carbon dioxide or nitrogen.

These specifications are somewhat more elaborate than the usual practice in sales of vitamin oils in the open market. There the producer submits samples of a lot of oil to interested buyers, who examine the sample as they see fit. If it meets their standards an offer is then made. However, the various tests, limitations, etc., listed under the War Food Administration sales contract are typical of the information the buyer may want to know about any vitamin oil. The ratios of the $E \frac{1\%}{1\ cm.}$ values at the two points on the absorption curve before and after the maximum point (328 millimicrons) to the value of $E \frac{1\%}{1\ cm.}$ at the maximum point have significance only in those cases where an oil from old or badly decomposed livers is being assayed. They are not used to any extent by private purchasers, but W. F. A. purchases included this factor to weed out certain grades of shark liver oils. There are indications that liver oils falling outside the specified ratio limitations are likely to be subject to considerable loss of potency from oxidation if stored for any prolonged period, and also that the biologically determined potency is likely to be significantly less than that indicated spectrophotometrically. Since W. F. A. supplies were often moved long distances under storage conditions that were far from ideal, any test that would help insure the

quality of the vitamin oils at the users' end of the transaction was of considerable value.

Stability of Vitamin A

There has been a rather extensive study of the factors that are responsible for the loss in the vitamin A content of fish liver oils between the time of extraction and the time of consumption. The opinions, theories, and reports in the literature are often somewhat at variance. One difficulty has been that the conditions for one experiment have been sufficiently different from those in another that no direct comparison of the results may be made. A discussion of some of the factors investigated, with brief summaries of research reported, will suffice to bring out the characteristics of the problem of maintaining the stability of the vitamin A content of fish liver oils.

On the basis of the reports published, some of the factors believed to contribute to the destruction of vitamin A are oxidation, hydrolysis, and the action of micro-organisms. If the oil has been properly prepared and stored, micro-organisms should not be a serious problem. The other factors, which have a more direct bearing on oxidative changes, will be discussed.

The destructive effects of light on vitamin A were recognized early (20) and precautions were taken to use brown glass containers or otherwise exclude direct or indirect sunlight from bottled cod liver oil. As an example of the magnitude of the losses from the effect of direct and indirect sunlight, one investigation (21) reported destruction of 80 percent of the vitamin A in an oleovitamin A and approximately 40 percent of the vitamin A in cod liver oil after 11 days under comparable storage conditions.

The action of oxidative agents on the vitamin A in fish oils has been explained in several ways. One theory is that, in marine animal oils -- and in vegetable oils -- there are substances normally present which act as antioxidants. Some of these antioxidants may be sterols with a free OH group. One of the principal natural antioxidants that has been identified in fish liver oils is alpha-tocopherol. The oxidation of oils is thought to be an antocatalytic chain reaction in which a series of intermediate products are formed. The constituents of the oil first combine with oxygen to form "moloxides" which are defined as peroxide compounds of unknown composition and structure. These "moloxides" or the more stable peroxides may react to form aldehydes which in turn autooxidize, first to peracids, then to acids. When antioxidants are present in the oil, they act to break this chain reaction by destroying the

(20) Holmes, A. D. and M. G. Pigott, 1926. Effect of Light on Vitamin A Content of Cod Liver Oil. Boston Med. Surg. J. 195, 263-265.

(21) Holmes, A. D. and M. G. Pigott, 1942. Comparative Stability of Vitamin A in Cod Liver Oil. J. Am. Pharm. Assoc. 31, 521-523.

"moloxides" and peracids formed. In so doing, however, the antioxidant is used up or converted to an inactive form. During the induction period, the antioxidant breaks the chains almost as rapidly as they are formed. As soon as all the antioxidant has been used up in this process, the oxidative changes of the chain reaction then continue at the normal, high rate. The oil becomes rancid, and the vitamin A is oxidized to a form not available for use by the animal body. Measurements of the absorption of the ultra-violet light in the spectrophotometer may indicate that an oxidized oil still has vitamin content, but the bioassay usually will not confirm these measurements of vitamin A value.

For any given sample of oil of unknown history, a single peroxide estimation is practically meaningless. If, on the other hand, a series of peroxide tests are made over the storage life of this oil, the shape of the curve of the peroxide value versus time has significance. An oil from fresh livers, tested immediately after recovery, would be expected to have a very low peroxide value, especially since any small amount of peroxides present should have been removed during the heating process incidental to the oil recovery. As the oil ages in storage, oxidation will take place at some rate governed by several factors mentioned elsewhere in this report. Normally, the natural antioxidants in the oil act to take up oxygen for a time, as described above; and the peroxide values remain fairly constant or gradually begin to rise slowly. As soon as the antioxidants are exhausted, the peroxide value rises sharply. In many oils the peroxide value rises to a maximum and then declines almost to zero.

Obviously, unless such a study is made of a given oil, its relative stability may not be accurately determined. For example, in the alkali digestion or alkali refining of livers and liver oil, a portion of the sterols that act as natural antioxidants may be removed. The recovered oil may then have a shorter induction, or protection, period than if it had been prepared in such a manner that a lesser amount of the antioxidants would have been removed.

Simons, Buxton, and Coleman (22) stored several commercially prepared liver oils in open vials, at 95° F. (35° C.) and at room temperature, for 400 hours and measured the peroxide formation. They then compared the formation of peroxides with the loss of vitamin A. They reported that the higher the peroxide value, the greater the loss of vitamin A, and that for the other samples of the same oils stored at the lower temperature there was less loss of vitamin A for the same peroxide value. The liver oils studied were arranged into two groups: group one consisted of the less saturated oils and contained liver oils from cod and pollock and the U. S. P. Reference oil; group two consisted of the more saturated oils and contained the liver oils of halibut, grayfish, and swordfish. In group one there was the most destruction of vitamin A.

(22) Simons, E. J., L. O. Buxton, and H. B. Coleman, 1940. Relation of Peroxide Formation to Destruction of Vitamin A in Fish Liver Oils. Ind. Eng. Chem. 32, 706-708.

From the study, these workers concluded that the destruction of vitamin A increases with the unsaturation of the liver oils. Factors other than instability were said to influence the oxidative rate, since some of the most unstable oils occurred in group two.

Robinson (23) offers the hypothesis that the changes found to occur during the oxidation of a vitamin A concentrate by atmospheric oxygen at 100° C. can best be explained on the assumption that the following reactions occur more or less simultaneously: (1) addition of oxygen to any or all of the double bonds with formation of peroxides, which are immediately converted into other substances; (2) disruption of the peroxides giving aldehydes and ketones (and possibly also cyclic ethers and oxygen); (3) polymerization of the peroxides with unsaturated linkages; (4) oxidation of the alcohol group giving an aldehyde.

Ferrous iron catalyzed the oxidation process, but certain substances containing an OH group delayed oxidation or were antioxidants, according to Mattill (24).

The effect of activated carbon on the oxidative destruction of vitamin A in shark, halibut, and tuna liver oils was investigated by Buxton (25). The liver oil was added to a de-aerated mixture of carbon and solvent. After these materials had been stirred for 30 minutes, the carbon was filtered out and the solvent was distilled from the filtrate. The refined liver oil was then stored in completely filled, closed vials until the tests were conducted.

There was no immediate effect on the oxidative destruction of vitamin A as measured by peroxide values, but the induction period was shortened, and ultimately the oxidation rate was faster than for the control oil. He concluded that for oils exhibiting no induction period a depletion of the natural antioxidant has occurred in the processing or purification of the oil and that the presence or absence of the antioxidant is a major factor in the resistance of the oil to atmospheric oxidation, which in turn governs the rate of destruction of vitamin A.

The antioxidant content of fish livers apparently varies with species, among other things. Robeson and Baxter (26) removed and measured the vitamin E from the liver oils of the Mangona shark and the soupfin shark. They reported that the Mangona shark oil contained 0.01 percent of this antioxidant. Soupfin-shark liver oil, on the same basis, contained 0.04 percent of the antioxidant.

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(23) Robinson, F. A., 1938. Stability of Vitamin A and D to Oxidation. Biochem. J. 32, 807-814.

(24) Mattill, H. A., 1927. Oxidative Destruction of Vitamin A and E, and Protective Action of Certain Vegetable Oils. J. Amer. Med. Assoc. 89, 1505-1508.

(25) Buxton, L. O., 1942. Effect of Carbon Treatment on Fish Liver Oils. Vitamin A Destruction and Peroxide Formation. Ind. Eng. Chem. 34, 1486-1489.

(26) Robeson, C. D. and J. G. Baxter, 1943. Alpha-tocopherol, a Natural Antioxidant in Fish Liver Oil. J. Am. Chem. Soc. 65, 940-943.

Smith (27) reported that the loss in vitamin A content of fish liver oils was proportional to the peroxide value for the oil and that this loss was independent of the nature of the oil.

The benzenetriols, gallic acid, and ethyl gallate were found to be effective antioxidants for animal and vegetable fats by Golumbic and Mattill (28). These workers suggested that the natural antioxidants present in vegetable oils were reinforced by the addition of phosphoric or tartaric acids. Oils so treated were then more effective as antioxidants when added to animal oils.

Holmes et al (29) stored, at room temperature and at elevated temperatures, a series of samples of cod liver oil and halibut liver oil to which hydroquinone and lecithin had been added in varying concentrations. The protection factor was said to be a function of the concentration of the antioxidants. A synergistic effect was noted in those cases where a combination of the two compounds was added.

The losses of vitamin A in mixed feeds have been investigated rather extensively. There are several different factors that enter into this phase of stability that do not always apply for vitamin oils stored as oils. For example, the dispersion of the oil in the mixed feed increases the surface exposed to oxidative action. Some of the feed ingredients may act as antioxidants, while others seem to catalyze the destruction of vitamin A.

Bethke, Record, and Wilder (30) found that the addition of 0.1 percent of hydroquinone to the cod liver oil subsequently incorporated into a mixed feed for poultry did not decrease the losses of vitamin A during a storage period of six months at room temperature. Losses of vitamin A amounted to approximately 75 percent at the end of this storage period.

Holder and Ford (31) tested the stability of vitamin A (cod liver oil) at several potency levels in mixed feeds. These feeds were stored in burlap bags at 70 - 80° F. (21 - 27° C.) for 60 days. Some deterioration of vitamin A was noted after chick tests of these stored meals had continued for 10 weeks.

Previous reports that there is a progressive loss of the vitamin A supplied by fortified cod liver oil in mixed feeds were confirmed by tests

(27) Smith, E. L. 1939. Action of Peroxides on Vitamin A. Biochem. J. 33, 201-206.

(28) Golumbic, C. and H. A. Mattill, 1942. Antioxidant Properties of Gallic Acid and Allied Compounds. Oil and Soap 19, 144-145.

(29) Holmes, H. N., R. E. Corbet, and E. R. Hartzler, 1936. Lecithin and Hydroquinone as Antioxidants for Vitamin A. Ind. Eng. Chem. 28, 133-135.

(30) Bethke, R. M., P. R. Record, and O. H. M. Wilder, 1939. Stability of Carotene and Vitamin A in Mixed Rations. Poultry Sci. 18, 179-187.

(31) Holder, R. C. and S. K. Ford, 1939. Stability of Vitamin A in Mixed Feeds. Poultry Sci. 18, 345-349.

(32) of feed stored in burlap bags for 25 weeks at summer temperatures. At the end of 12 weeks of storage some 50 percent of the vitamin A had been destroyed.

Manganese sulphate, in the amount of 0.5 percent, added to a mixture of bran and cod liver oil, was found by Miller and Joukovsky (33) to exert a drying action on the oil with a concomitant destruction of vitamin A.

Many of the antioxidants suggested for use with vegetable and animal oils have not been so satisfactory for fish oils. For example, Lundberg, et al (34) reported that the addition to lard of nordihydroguaiaretic acid in a concentration of 0.01 percent gave a protection factor of 18. Studies at this laboratory indicated that this antioxidant in 0.05 percent concentration would afford a protection factor of approximately 3 when added to salmon body oil. The use of as much as 0.10 percent nordihydroguaiaretic acid increased the factor to only 6. At concentrations higher than this the bitter flavor imparted to the oil by the antioxidant interfered with the organoleptic tests for rancidity.

The Food and Drug Administration would have to pass on the use of any antioxidant in foods entering interstate commerce. Many of the compounds investigated as possible antioxidants have not yet been so approved.

Methods for Measurement of Vitamin A

Biological Assay

Physico-chemical methods are often used for the assay of vitamin A oils. The potency is declared in International or U. S. P. units; therefore, if any question arises as to the correctness of the declaration, settlement can be demanded on the basis of an official bioassay as outlined in the U. S. P. XII.

This assay is, essentially, a comparison of the rate of growth during a 28-day period of a series of groups of young rats receiving a prescribed diet plus measured amounts of the oil being tested with the rate of growth of another series of groups receiving an official standard preparation. Before the test feeding is begun, the rats are conditioned by being restricted to a diet free of vitamin A for a sufficient time (20 - 45 days) to cause them to manifest evidence of vitamin A deficiency characterized by declining weight and/or ophthalmia.

(32) Baird, F. D., A. T. Ringrose, and M. J. MacMillan, 1939. Stability of Vitamin A in Mixed Feeds. Poultry Sci. 18, 441-448.

(33) Miller, W. and V. Joukovsky, 1942. Effect of Manganese Sulphate on the Stability of Vitamins A and D in Mixed Feeds. Poultry Sci. 21, 200-202.

(34) Lundberg, W. O., H. O. Halverson and G. O. Burr, 1945. The Antioxidant Properties of Nordihydroguaiaretic Acid. Oil and Soap 21, 31-35.

The international unit of vitamin A has been fixed as the potency of a definite weight, 0.6 micrograms, of purified beta-carotene. The international standard preparation is made up of beta-carotene dissolved in a vegetable oil at such concentration that one gram of the solution contains 0.3 grams of beta-carotene. In every two micrograms of the International Preparation then, there is contained one International Unit of vitamin A.

In 1934, at the international conference on vitamin standardization, sponsored by the League of Nations, it was proposed that a subsidiary reference standard be established for bio-assays of vitamin A. The suggested material for this purpose was the Reference Cod Liver Oil of the United States Pharmacopoeia which had been used as a standard for vitamin A assays in the United States for several years. A quantity of this Reference Cod Liver Oil was placed at the disposal of the Health Organization of the League of Nations; and, after a series of collaborative assays against the International Carotene Standard, this subsidiary standard, known as U. S. P. Reference Oil 1, was accepted at the potency of 3,000 I. U. of vitamin A per gram of oil. From time to time new lots of Reference Oils have been issued as U. S. P. standards.

The Vitamin Committee of the American Oil Chemists' Society (35) has recommended that a combination of a vegetable oil and crystalline vitamin A acetate be accepted as a standard. The following tabulation was made showing the desirable properties of their suggested standard.

Vitamin A Reference Standard

Property	Physicochemical Requirements	Biological Requirements	Committee's Present Opinion
Form of Vitamin A	The substance $C_{20}H_{29}OH$ or ester	Same	Pure vitamin A acetate
Concentration	As high as possible to give little interference with physicochemical tests	As low as possible to simplify dilution with carrier oil	3,000 micrograms of $C_{20}H_{29}OH$ per gram (about 10,000 U.S.P. units/gram)
Diluent	A non-volatile oil which will not interfere with physicochemical tests	A non-volatile oil which will not interfere with biological tests	Refined and deodorized cottonseed oil
Antioxidant	Must be oil soluble and not interfere with physicochemical tests	Tocopherol	1 to 3 mg. of tocopherol/g. (perhaps the natural content of cottonseed oil will be sufficient)
Container	Ampoule or capsule opaque to actinic light	Same	One-piece gelatin capsules

(35) Embree, N. D., 1946. Report of the Vitamin Committee 1945-46. Oil and Soap 23, (9), 275-276.

Because biological assays are rather costly and require considerable time, commercial firms have generally adopted physicochemical methods for the estimation for trade purposes of the vitamin A content of liver oils. The biological activity of the vitamin A present is, of course, the ultimate assay criterion.

Antimony-Trichloride Color Reaction Test

Numerous workers have sought to measure the vitamin A content of liver oils by some chemical means. The Carr-Price (36) method, involving the reaction of antimony trichloride to give a characteristic blue color whose intensity is directly proportional to the amount of vitamin A present in the sample, is one of the most realiable and widely used of these tests. A 20 to 25 percent solution of antimony trichloride in chloroform is added to a chloroform solution of the oil to be tested. The blue color that develops is measured in a colorimeter or by spectrophotometric analysis. By means of data gathered from the measurement of the color developed by an oil of known potency at various dilutions, a graph is prepared from which the potency of the unknown sample can be computed; or a conversion factor can be used whereby the value of $E\ \frac{1\%}{1\ cm.}$ 620 millimicrons is converted directly to units of vitamin A. This method is relatively easy to use, requires very little time, and, if properly done, may usually be accurately correlated with biological assay values. For oils of low potency, it is recommended that the unsaponifiable portion be used, rather than the whole oil, if accurate results are desired.

Physical Methods

The vitamin oil industry in the United States has adopted the determination with a spectrophotometer of the extinction coefficient ($E\ \frac{1\%}{1\ cm.}$) for light of 328 millimicrons in wave length as the accepted physical method for assaying vitamin A oils for trading purposes. In its simplest terms, this method is based on the measurement, by means of a photoelectric cell and an electric meter, of the amount of light transmitted by a solution of the oil. Vitamin A has the property of absorbing the specified wave band of ultraviolet light in an amount which is a function of the quantity of vitamin present in the solution. If we standardize the meter readings by making a series of measurements with various dilutions of an oil of known potency, the potency of an unknown oil may then be calculated from its transmission readings.

The technique of operations, the preferred solvents, and the other conditions of the test have been fairly well standardized. The vitamin content of the material being tested is calculated by multiplication of its value of $E\ \frac{1\%}{1\ cm.}$ 328 millimicrons by a conversion factor. The conversion factor of 2000 is now usually used in the United States, but in some countries other values, such as 1600 are used.

(36) Carr, F. H. and E. A. Price, 1926. Color Reactions Attributed to Vitamin A. Biochem. J. 26, 498.

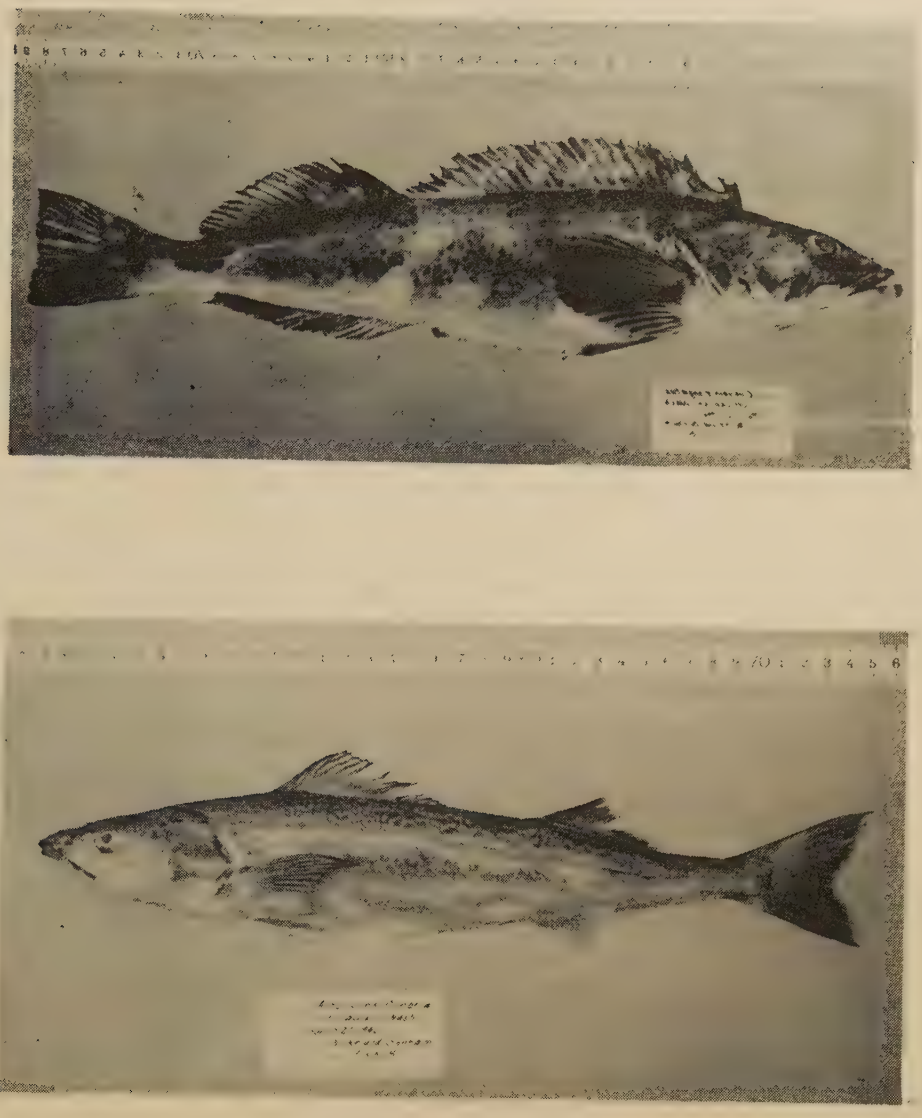

Figure 24. Upper photo, the Lingcod, (Ophiodon elongatus). Lower photo, the Sablefish, (Anoplopoma fimbria).

The Vitamin Committee of the American Oil Chemists' Society (37) has proposed a method for the physicochemical assay of vitamin A. The outline os this method is given below. Since some of the points mentioned are still in dispute, the committee intends to conduct further experimental work before the tentative method is accepted as official.

(37) American Oil Chemists Society (1946). Report of the Vitamin Committee 1945-46. Oil and Soap, 23: 275-276

Tentative Method for the Physicochemical Assay of Vitamin A

	Procedure	Detail
Basic Method	Determination of extinction coefficient at 326 to 328 millimicrons; calculate vitamin A content by direct proportion.	Solvent to be isopropanol. Calibrate instrument with new vitamin A standard. Report in gravimetric units.
Necessary confirming data	(I) Determination of extinction coefficients at 300 and 350 millimicrons.	The ratios, E (300)/E(328) and E (350)/E(328), to have values in prescribed ranges.
	(II) Determination of depth of color, at 620 millimicrons, of $SbCl_3$ reaction product; potency to be calculated by comparison with color produced by vitamin A standard.	Potency to be determined by comparing reaction product of test solution with that of test solution fortified with standard. The color of the reaction product must fade at a prescribed rate. The potency by the color method must agree (within prescribed tolerance) with potency by ultraviolet method.
Purification Methods	(I) Saponification	Probably will be required.
	(II) Distribution between solvents.	Might be optional.
	(III) Chromatography of unsaponifiable fraction	Might be optional.
	(IV) Molecular distillation.	Might be forbidden, except under conditions that would prevent pyrolysis of kitol into vitamin A.

International and U. S. P. Standards for Vitamin A

Rosenberg (38) lists the inter-relationship of the various vitamin A units used as follows:

> One I. U. (International Unit) = One U. S. P. unit; one I. U. = 0.6 micrograms of pure beta-carotene, m.p. 184° C., optically inactive, dissolved in coconut oil with addition of hydroquinone; one I. U. = 1.5 to 2 Sherman units.
>
> One gram of U. S. P. cod liver oil must contain at least 600 U. S. P. units of vitamin A. (Since July 1, 1940, a minimum of 850 units per gram is required.)
>
> One gram of pure vitamin A contains 4,500,000 International Units.
>
> One Cod Liver Oil Unit (C. L. O. Unit)
> = 125 gamma (*) of beta-carotene
> = 208 U. S. P. Units
> = 10 "Lovibond Units"
> = 50 Lovibond units (Wolff)
> = 550 blue units (Moore)

In British practice, one International Unit of vitamin A is in effect defined by $E\ \frac{1\%}{1\ cm.}$ 328 millimicrons = 0.000625, which is equivalent to the use of 1600 as conversion factor for the physical measurement value. In the United States the conversion factor of 2000 is usually used instead of 1600.

Wartime Price Structure for Vitamin A

The price of vitamin A in fish liver oils has varied over a rather wide range from time to time as the supply and demand situation has changed. During the past few years, the large demand and the short supply of vitamin A oils caused most sales to take place at or near the maximum ceiling prices set by the Office of Price Administration (39). For the purposes of price regulation, two classifications were set up for domestic oils: 1) vitamin A natural oils, and 2) vitamin A concentrates. Oils imported from foreign sources were subject to the same maximum prices F. O. B. the U. S. trans-continental rail shipping point with duty and taxes to be paid by the seller.

a) Vitamin A natural oils, that is the oils as they are processed from the liver, etc., without any form of concentration being employed, were sold by potency groups as follows:

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(38) Rosenberg, H. R. Chemistry and Physiology of the Vitamins. p. 83, Interscience Publishers, Inc., New York, N. Y. 1942.

(*) 1 gamma = 10^{-6} grams.

(39) Maximum Price Regulation No. 203, Vitamin A Natural Oils and Concentrates, Amendment No. 1.

Potency in U. S. P. Units of Vitamin A per Gram	Maximum Price per Million U. S. P. Units of Vitamin A
Less than 40,000 (*)	14 cents
40,000 and over but less than 200,000.	14 cents plus one-tenth of a cent for each potency increment of 1,000 U. S. P. units of vitamin A per gram in excess of 40,000.

b) The maximum price of vitamin A concentrates from any source or method was 30 cents per million U. S. P. units of vitamin A.

Maximum prices for fish body oils, such as sardine, menhaden and herring oils, for use in animal and poultry feeding were not fixed by this schedule. These oils continued to be sold as marine animal oils under the following ceilings:

Sardine oil, crude, f. o. b. producer's plant, Pacific Coast - 8.9 cents/pound.

Menhaden oil, crude, f. o. b. producer's plant, Atlantic Coast - 8.9 cents/pound.

Herring oil, crude, f. o. b. Seattle - 8.9 cents/pound.

No maximum price schedule was set up for fish livers except in the Alaska area. For a time this lack of balance for vitamin oil ceiling prices was a source of some controversy, but no action was taken. There gradually developed a trend toward the replacement of "blind buying" by the purchase of livers on the basis of samples and assays. If a purchaser so desired, he could pay more than the ceiling price for the vitamin in the livers; but only those dealers who could incorporate the oil into final products to make up the added cost of raw materials resorted to such practices. At present the prices of livers are meaningless without the accompanying data on vitamin A content per pound of liver, but the schedule of prices as fixed in Alaska will serve as a rough approximation of the value placed on fish livers in 1944.

	Maximum price per pound
Halibut livers	$1.30
Sablefish livers	1.65
Lingcod livers	2.00
Rockfish livers	0.75
Halibut and Sablefish viscera	0.25
Skate livers	0.10
Dogfish livers	0.15
Mudshark livers	0.25

(*) Oils sold as vitamin oils were covered by the ceiling to the lowest possible content of vitamin A.

By way of comparison, the announced rates of payment per pound to members of the Canadian United Fishermen's Cooperative in 1944 were:

	Average price per pound
Halibut livers, area 2	$0.42
Halibut livers, area 3	1.30
Halibut viscera	0.16
Lingcod, outside pool	2.65
Lingcod, Gulf pool	1.75
Lingcod, Kyuquot pool	1.65
Red Cod and Sablefish	1.50
Soupfin, Vancouver pool	4.20
Soupfin, Skidegate pool	4.10

VITAMIN D

Some fish oils are used as sources of vitamin D. The vitamin D may be stored in the body oil, as in the herring (around 100 I. U. per gram), or in the liver, as in the percomorphs. The amount of the vitamin present varies with species, season, maturity, etc.; but a few typical examples, as given in Table 5 in the appendix, will show the general range of potencies, in I. U. per gram of oil, by species.

The liver oils from the percomorphs, halibut, and cod are used as a source of vitamin D for humans. Fish body oils, cod liver oil, and other fish liver oils are employed in animal and poultry feeding. The natural vitamin D is made up of several distinct compounds. In fish liver oils, the activity is thought to be largely due to vitamin D in the form of activated 7-dehydrocholesterol (D_3). In some instances fish liver oils have exhibited as much as three times the activity that could be attributed to the 7-dehydrocholesterol content of the particular oil. One possible explanation of this phenomenon is said to be that such oils contain an as yet unidentified member of the vitamins D.

Another commercially significant form of vitamin D is irradiated ergosterol, called calciferol or D_2 when in a purified and concentrated form. The relative activity of these two forms of vitamin D in different organisms is worthy of note. Poultry apparently utilize D_2 to a very limited degree, while rats are able to utilize D_2 about as well as D_3. Vitamin D_3 gives a very good chick activity response. The relative utilization in humans is not well understood as yet.

Measurement of Vitamin D

Some physical methods have been suggested for the assay of vitamin D. The characteristic absorption spectrum maximum at 265 millimicrons is sometimes used, but only relatively pure vitamin D may be reliably evaluated by this method, since other substances usually present in fish oils have similar absorption spectra. However, the biological assay must be depended upon at present.

Bio-assays for vitamin D are conducted with rats or chicks. The rats respond equally well to D_2 and D_3, but the activity so measured is not necessarily applicable to chicks. Chicks seem to require D_3 for best bone formation. Standard practice for reference purposes has been to follow the rat assay method as outlined in the U. S. Pharmacopoeia or the chick assay method of the Association of Official Agricultural Chemists.

Rat Assay

Rats are fed a ration deficient in vitamin D and containing an abnormally high ratio of calcium to phosphorus for a period of 18 to 25 days in order to induce rickets. The rats showing evidence of rickets are divided into several groups. One control group is fed, in addition to the depletion diet used to this point, a daily dose of a standard reference oil. One or more other groups of these rats are fed the depletion diet plus the oil being assayed. Usually it is necessary to use several levels of dosage of the assay oil, unless the potency is known within rather narrow limits. After the vitamin oils have been fed in known daily dosages for six days, the reference and assay groups are returned to the depletion diet for two days. All the rats are then killed; and the degree of healing of the rachitic condition induced by the oil being assayed is compared to that induced by the standard reference oil. The leg bones after being sectioned, washed, immersed in silver nitrate solution, and irradiated are examined to determine the degree of healing, as indicated by the amount of calcification.

Chick Assay

The chick assay for vitamin D has been standardized by the Association of Official Agricultural Chemists. The assay is similar to that for rats, except that no depletion period is necessary. Chicks one or two days old are started directly on the test. One or more negative control groups receive no vitamin D, three or more positive control groups receive graduated levels of U. S. P. standard reference cod liver oil, and one or more groups receive the assay oil. The assay period is 21 days. At least 15 chicks must remain in each group at the end of the test.

After the chicks have been killed, the left tibia of each chick is freed of tissue, solvent extracted to remove all fat, dried to constant weight, and ashed. The percentages of ash in the tibias of the assay groups are then compared to the percentages of ash obtained from the tibias of the reference groups, and, by means of the relative amounts of oil used, the potency of the unknown sample may be estimated (40). Potencies of oils assayed by this method are expressed in A. O. A. C. chick units of vitamin D per gram of oil. Poultry feeders usually demand this form of report to insure proper activity of the vitamin D in their feed mixtures.

A somewhat modified form of the chick assay is also used in which the bony portion of a toe is ashed instead of the tibia. Since the chicken is not killed in this instance, further tests and observations may be

(40) Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists. Six Edition, 625-626, 1945.

made on the same individual if they are thought desirable. Some companies then use these same chicks for tests of feed rations, etc.; and ultimately the birds may be sold for consumption to defray part of the expenses of the testing laboratory.

A thorough discussion of the various potency levels and ingredients that are used for animal and poultry feeding oils was given in the previous section entitled Distribution of Finished Oil.

FUTURE SUPPLIES OF VITAMIN A

During the war, there was a tremendously increased demand for vitamin A. In order to meet this demand, the seas were searched to uncover new species of fish that could be utilized and to increase the supplies of raw materials from species already being exploited. As a result of this activity, certain observations have been made that have a bearing on the future supplies of vitamin A.

The intensive activity in the fisheries for soupfin shark, Mexican shark, mud shark, and grayfish has led to diminishing returns per unit of effort which indicate some depletion of these populations. As previously mentioned, several companies procure part of their fish livers and oils from foreign sources. A more complete discussion of foreign developments will be included below.

In contrast to the possibility of lessened yields of vitamin A from marine sources, there is some chance that more vitamin A may be produced from plant carotene or by chemical synthesis. Because such developments would have repercussions within the commercial fishery, they will be enlarged upon here.

Synthetic Vitamin A

In the early stages of research into the nature of the compound that was later identified as vitamin A, a similarity was noted between beta-carotene and vitamin A. As studies progressed, the theory was advanced that the beta-ionone ring was essential for vitamin A activity. As early as 1932, attempts were made to snythesize vitamin A with beta-ionone as the starting material. These early preparations, upon assay, showed a high degree of activity; but subsequent attempts to duplicate the synthesis resulted in no such materials. It is supposed that the methods for measurement of vitamin A were not of the best and that the true potencies were probably less than those reported.

For the next 10 years efforts were continued to develop a satisfactory process for this synthesis. Workers in many countries reported varying degrees of success in laboratory experiments, but the problem of a practical commercial process remained unsolved. Patents have been issued covering some of these methods. A typical patent was granted to Kuhn and Morris (41) in 1941. Their process involves the condensation of Beta-ionylidene

(41) Kuhn, R. and Morris, C. J. O. R., 1941. U. S. patent 2,263,375. Synthesis of Vitamin A.

acetaldehyde with beta-methylcrotonaldehyde and a reduction of the aldehyde and a reduction of the aldehyde group of the latter to the alcohol group. Details of the procedure for accomplishing this synthesis are given in the patent.

In 1942, Dr. Nicholas Milas (42) of the Massachusetts Institute of Technology filed an application for a patent on the snythesis of vitamin A. In 1945 a number of patents, including number 2,369,156, were granted him covering a process of synthesis starting with beta-ionone. A perusal of these patents brings out very clearly the complications involved to put the vitamin A molecule together synthetically. The second Milas patent mentioned required some 12 intermediate steps. Apparently, despite the extensive efforts expended, vitamin A will still have to come from natural sources during the immediate future.

Arens and van Dorp (43) reported from Holland the synthesis of compounds possessing vitamin A activity. They used beta-ionone as the starting point, reacting it with gamma-bromocrotonicester and zinc in benzene. Subsequent processes of dehydration, saponification, conversion to the ketone, reaction with bromoacetic ester and zinc in benzene, and dehydration with anhydrous oxalic acid, followed by saponification resulted in a substance exhibiting strong vitamin A activity. These workers proposed the name "vitamin A acid" for this compound.

Carotene

The animal organism can utilize various carotenes from fresh plant materials as provitamins from which vitamin A is manufactured in the body. The degree of activity of the carotenes varies somewhat, but they are all considerably less active than vitamin A. The International Unit of beta-carotene and of vitamin A are of equal value only under the specified conditions of the bio-assay previously described and are not equally effective in the metabolism of the normal growing organism according to Guilbert, et al (44). These workers found also that animal needs are 40 I. U. of beta-carotene or 20 I. U. of vitamin A per kilo of body weight, for minimal requirements of normal growth. If adequate storage for reserve and for reproduction is to be built up, 60 I. U. of vitamin A or 200 I. U. of beta-carotene are needed. On this basis, the average adult needs 5,000 or 15,000 units, respectively, while adolescents, pregnant women and nursing mothers require more (45).

Sherwood and Fraps (46) found that birds and fowls have need for vitamin A or carotene. For example, growing chicks require 1800 I. U. of

(42) Milas, N. A., 1942. U. S. patent 2,382,085. Synthesis of Vitamin A. Assigned to Research Corporation.

(43) Arens, J. F. and D. A. van Dorp, 1946. Synthesis of Some Compounds Possessing Vitamin A Activity. Nature 157, 190-191.

(44) Guilbert, H. R., C. E. Howell and G. H. Hart, 1940. Minimum Vitamin A and Carotene Requirements of Mammalian Species. J. Nutrition 19, 91.

(45) Irving, J. T. and M. B. Richards, 1939. Influence of Age on Requirements of Vitamin A. Nature 144, 908.

(46) Sherwood, R. M. and G. J. Fraps, 1936. Quantities of Vitamin A Required by Growing Chicks. Texas Agr. Exptl. Sta. Bull. M528.

vitamin A per pound of feed. In terms of carotene, this is equivalent to 95 to 125 micrograms per day. Laying hens require 200 to 500 micrograms of carotene daily.

There is apparently some difference in the efficiency with which different species convert carotene to vitamin A. Rats were found by Baxter and Robeson (47) to utilize beta-carotene only half as well as they did vitamin A from marine sources. Several other workers (48) rated animals in the order of their ability to convert carotene, starting with the rat as highest, followed in order by chickens, guinea pigs, rabbits, pigs, and cattle. Cats could not convert carotene to vitamin A.

Nelson and Moore (49) reported that calves raised without access to milk of an adequate vitamin A content require a supplement of fish liver oil since the calf does not utilize carotene from hay or other vegetation before the age of five months.

There is as yet no definite demonstration of the efficiency with which man can utilize carotene.

Carotene concentrates are at present available for fortification of feeds and foods. The prices are on a competitive level with vitamin A concentrates, approximately 30 cents per million U. S. P. units. During the period of short vitamin A supply there has been some thought given to the substitution of this carotene concentrate for vitamin A. Margarine manufacturers, for example, could use the carotene to advantage except that the bright yellow color imparted to the product might render such margarine subject to tax as being artificially colored. One disadvantage of carotene concentrates is that their dilution to lower potencies may be relatively expensive because of the added cost of the carrier or diluting oil.

With the present state of information, most users will probably continue to safeguard their feeding rations and other products by the addition of true vitamin A. As more data become available on the relative content and the efficiency of conversion of carotenes in common feed stuffs, the rational approach is to supplement with true vitamin A only to the level required for optimum results. Such an action will assist materially in the proper conservation of fish liver oils so that a sufficient supply will be available for those uses in which the carotenes are not suitable.

Beta-carotene may be made commercially from fresh plant materials, such as carrots and grass crops, or from vegetable oils, such as red palm oil. A brief description of a process suitable for use with carrots will show the general principles involved.

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(47) Baxter, J. G. and C. D. Robeson, 1940. Crystalline Vitamin A Palmitate and Vitamin A Alcohol. Science 92, 202.

(48) Moore, L. A., 1932. Notes on Conversion of Carotene to Vitamin A in Cows. Biochem J. 26, 1.

(49) Nelson, H. F., L. A. Moore, R. E. Harwood and G. A. Branaman, 1945. Vitamin A or Carotene for Calf Feed. Flour and Feed 46. No. 6, 24.

The first step required is the removal of most of the moisture. If the carotene content is to be protected, the moisture should be removed as rapidly as possible and at minimum temperatures. Vacuum evaporation or dessicants, such as anhydrous sodium sulphate or alcohol, may be used. The dry material is next treated with a suitable solvent, such as benzene or acetone, to remove the fat and carotene. The final separation of the carotene concentrate from the fat is accomplished by a saponification process in which excess alkali and high temperatures are avoided to protect the carotene. Materials such as carrot juice may be used for carotene manufacture. The juice is either heated or treated with acids to coagulate the protein. The carotene is adsorbed by the coagulation protein, and the extraction process thereafter is as described above. For animal feeding, very often the dried green material or the crude fat concentrate is used without additional refining. Some justification for the presence of the fat is indicated by the reports of several workers that a more satisfactory conversion of carotene to vitamin A takes place when poultry are fed a ration of higher fat content (50).

FOREIGN DEVELOPMENTS

Canada

As was mentioned in another section, the cod liver oil industry has for many years been of some importance on the eastern coast of Canada. Before the war, Canada produced only a small part of its own cod liver oil requirements. For example, in 1938 the production was 60,000 gallons while the consumption amounted to 150,000 gallons. When war conditions shut off outside sources of supply, a cooperative effort on the part of the Dominion and provincial governments and of private industry resulted in the establishment of factories at Rimouski, Riviere aux Renards, and Paspebiac along the Gaspe peninsula in Quebec. Through this expansion, and by reason of the newer preservative and processing technique explained elsewhere in this report, the production of cod liver oil had been increased to 400,000 gallons, most of which was medicinal grade, in 1942.

An investigation (51) has been made of the population of grayfish off the Nova Scotia coast to determine whether the livers would be suitable as a vitamin A source. The potencies of the livers examined varied from 1,200 to 7,400 U. S. P. units of vitamin A per gram. There was some variation with season, size, and maturity but none with locality of capture. Reported recovery of oil by steaming was approximately 50 percent. Somewhat better yields were obtained by the alkali digestion method. On the basis of the tests made, the investigators decided the Atlantic grayfish did not offer a large enough vitamin A content to make recovery profitable.

(50) Russell, W. C., M. W. Taylor, H. A. Walker, and L. J. Polskin, 1942. The Absorption and Retention of Carotene and Vitamin A by Hens on Normal and Fat Rations. J. Nutrition 24, 191-211.

(51) Anonymous, 1944. Atlantic Coast Dogfish Livers. Canadian Fisherman 31, No. 4, 6.

Since the discovery of the valuable vitamin A oils supplied by halibut, lingcod, sablefish, grayfish, shark, etc., Prince Rupert and Vancouver, B. C., have become the major producing areas in the Canadian liver oil industry. Perhaps the most significant growth has been shown by fishermen's cooperatives. In 1940, the Fishermen's Cooperative Association of Prince Rupert, which had previously dealt only in fish, constructed a fish liver processing plant there. Gradually the other member groups of the Fishermen's Cooperative Federation added their liver catches to the pool. In 1944, the group at Vancouver, the United Fishermen's Society, purchased the facilities of a company that had been processing livers for the Society on a contract basis. The Vancouver group by 1945 had built a new liver-processing plant the design of which was largely based on the experience of the Prince Rupert operations. By an agreement, all the livers brought in by members of the Federation were processed that year at the two plants.

There are seven other organizations processing livers in British Columbia. The companies that produce fish body oils blend these oils with the liver oils in order to market an animal and poultry feeding oil. The balance of the vitamin oils are sold directly to the pharmaceutical trade or to concentrators.

Figure 25. Grayfish aboard otter trawler. (Photo courtesy Pacific Fisherman).

The importance of the fish liver business to the province is brought out in the 1944 report issued by the Dominion fisheries department. The landed value of all fish livers, $3,480,000, was exceeded only by the landed value of salmon and of herring. The values of the livers by major species were: grayfish - $2,660,000; ling cod - $276,000; soupfin shark - $218,300;

halibut - $202,000. Other materials processed for vitamin A oils included livers of sablefish, rockfish, mud shark, ratfish, gray cod, skate and sole and also miscellaneous fish viscera.

Mexico

Exploitation of the shark populations off the west coast of Mexico has been very largely carried out by the Mexican subsidiaries of companies in the United States. When the fishery was first explored, the methods used were rather crude. Walford (52) has described a typical example. In sheltered coves along the coasts of the Gulf of California and along the Pacific coast of Lower California there are numerous shark fishing camps inhabited by small groups of fishermen or by individual families. Fishing equipment consists of a small dugout or a skiff and one or more skates of gear. The set line used is essentially a buoy line about 2,000 feet long with an anchor on the other end. At right angles to this line, and near the lower end, a second rope about 500 feet in length is fastened. At intervals of about 10 feet, ganging lines of 1/2-inch manila rope approximately 3 feet in length are secured to this rope. On the end of each ganging a swivel is placed and the large shark hook, having a shank a few inches in length, is connected to the swivel through a 2-foot length of chain. The hooks are baited and the line is cast overboard. After the gear has been set for one to three days, the fisherman hauls up the line by hand, removes any sharks and rebaits the hooks. The flanks, fins and livers are usually removed for preservation by drying, salting, or some chemical treatment. Periodically a journey is made to one of the larger ports where the shark products are sold to a dealer or a representative of some American processor. The salted or preserved shark livers are then sorted by the dealer; and when a shipment of sufficient size is on hand, he sends it by truck, rail, or boat to the company he represents.

Some of the disadvantages of this source of supply are obvious. Livers spoiled readily at the prevailing temperatures unless they were quickly and properly preserved by the fisherman. No accurate segregation was made by species; and, since potencies varied widely, the buyer offered a minimum price to cover possible losses. Improperly preserved livers yielded an oil that did not meet the trade specifications and was therefore difficult to sell.

As the Mexican people learned more about the shark liver business, many of these faults were corrected. The company that started at Guaymas in 1939 was moved to Mazatlan in 1940. A California corporation purchased the enterprise in 1942 and has operated it on a somewhat larger scale since then.

(52) Walford, L. A., 1944. Observations on the Shark Fishery in the Central Part of the Gulf of California with Records of Vitamin Potency of Liver Oils and with Keys to Identification of Commercially Important Sharks. Fishery Market News 6, No. 6, 3.

In 1944 (53) a company at Acapulco began a well-organized project to capture sharks in Mexican waters. The company arranged to furnish larger power boats, gear, and other required equipment for the fishermen, who were carefully instructed as to what potencies of vitamin A could be expected from different sources and how to care for the livers. Payment to the fishermen was to be based on the vitamin A content of the livers. A subsidiary of a company in the United States bought the salted livers and in turn shipped them to its processing plant.

During the early war period, the Mexican shark fishery supplied badly needed vitamin A; but, from the steady decline in production for the past two years, there is some indication that the local shark populations have been depleted by the intensive efforts of the fishermen.

Central America

Several of the major California liver processors have been seeking vitamin-bearing materials in Central America. Those companies which were obtaining tuna from these waters were in a good position to handle salted shark livers also at their foreign stations. The fishing methods, the vitamin content, and the methods of preserving the livers are generally similar to those described for the Mexican areas.

South America

For a number of years, and in accordance with law, the United States Government has been cooperating with the American Republics by detailing technically trained personnel (usually at the expense of the foreign governments) to investigate their fishery resources, and to suggest ways and means for the more efficient development, utilization and conservation of those resources. As a result of this increased activity, expecially during the war period, the production of food fish was somewhat increased. There was also a lively interest in the vitamin-bearing materials that might be available from these fisheries.

On the Pacific Coast, the Peruvian fisheries have become increasingly attractive to United States companies, who are establishing tuna and swordfish canneries and handling stations. These are usually operated through a Peruvian subsidiary or local representative. Some preserved fish livers have been exported to the United States, although the demand for vitamin products in Peru still remains unsatisfied. As facilities become available, it is probable that fish meals and body and liver oils may be supplied for domestic use to strengthen and build up the economy of the country.

Argentina, on the Atlantic Coast of South America, has been supplying shark livers and oils in increasing volume since 1943. Imports of shark liver oil to the U. S. were reported as 60,000 gallons in 1944. This was approximately equivalent to 20 percent of the shark liver oil produced on the Pacific Coast of the United States that year. The Argentine shark

(53) Anonymous, 1944. Vitamins from Mexico. Pacific Fisherman 42, No. 11, 59-60.

Figure 26. Soupfin-shark bottom net. (Photo courtesy Pacific Fisherman).

liver oils are usually within the potency bracket of 40,000 to 60,000 U. S. P. units of vitamin A per gram, although oils of over 100,000 units per gram are reported. The sharks captured in the first area exploited off Mar del Plata and Necochea, south of the La Plata estuary, are termed "Cazon" by the fishermen (54). These fish weigh approximately 20 to 24 pounds each, and their livers weigh approximately two pounds each. The average oil yield of these livers is estimated at approximately 70 percent. Fishing usually starts in May or June and continues through December. As a result of exploratory fishing, a second area off Punta del Este on the Uruguayan Coast has been discovered. Recently a shipment of shark liver oil was received in New York from Montevideo, Uruguay.

Various reports in the literature indicate that Uruguay, Chile, and Brazil are investigating the potential vitamin oil resource of their fisheries. The liver oils of sharks landed in these countries have often contained 20,000 to 50,000 U. S. P. units of vitamin A per gram. Chile has a large fishery for swordfish; and, if the liver oil potencies are comparable to

(54) Anonymous, 1946. Vitamin Production in Argentina. Norsk Medicinal Union, Bergen, Norway.

those from this species elsewhere (100,000 to 300,000 U. S. P. units of vitamin A per gram), this fishery will be a valuable source of vitamin A.

Caribbean Area

In the Caribbean area, shark livers have been taken in small quantities. Some preserved livers are exported to the U. S. from Cuba. Haitian fishermen are being encouraged to bring in shark livers so that vitamin oils may be recovered for local consumption. The fishery surveys in the Caribbean have indicated that the shark populations are somewhat scattered and sparse. Potencies of liver oils tested have been similar to those reported for sharks from the Florida coast, namely an average of 8,000 to 15,000 units with extreme limits of 35 to 35,000 units per gram of oil.

South Africa

South Africa began extensive research in about 1940 into the fishery resources of waters accessible to the fishermen of that country. Measurements and data were collected of: (a) vitamin content, (b) percent oil yield, (c) ratio of weight of liver and viscera to total body weight, and (d) seasonal variations in (a) and (b) for livers and viscera. Similar data was also obtained for fish body oils, head oils, etc. recovered by reduction plants. These data will serve to guide blenders of animal and poultry feeding oils in the utilization of vitamin oils so recovered. Since that time, the various species captured have been examined as sources of raw materials for meal, body oil, and liver oil. Through the cooperative efforts of industry and government, there were three factories processing fish livers in Capetown in 1943. The livers handled included those from food fishes, sharks, and inedible varieties taken by deep sea trawlers. Typical potencies reported were: dogfish 4,000 to 6,000; blue shark 15,000 to 30,000; kingklip 10,000 to 40,000; and stone bass 100,000 to 600,000 U. S. P. units of vitamin A per gram of oil. By 1945 the South African liver oil industry was producing an estimated 10 percent of the total vitamin A supplies of the United Nations (55).

Australia and New Zealand

Australia and New Zealand have not been as active producers as South Africa in the vitamin oil field, but studies are being made of the fishes in their waters. At least one factory has been processing livers at Auckland, New Zealand (56).

Wood (57) has suggested the following methods of processing as most suitable for the types of livers available in Australia: (a) for shark and ray livers--steaming; (b) for yellowtail and striped tuna livers and barracouta viscera--alkali digestion; (c) for bluefin tuna and other high vitamin content livers--alkali digestion with added oil to act as a solvent.

(55) Anonymous, 1943. Canadian Fisherman 30, No. 3, 24.
(56) Anonymous, 1944. Canadian Fisherman 31, No. 10, 8.
(57) Wood, B. A., and E. J. Ferguson, 1941. Commercial Production of Fish Liver Oils. J. Council Sci. and Ind. Research 14, No. 4, 311-314.

The Australian shark fishery has adopted the long-line gear previously described. The livers are shipped iced or frozen to Melbourne or Adelaide. Potencies vary somewhat but an average of 15,000 International Units of vitamin A per gram is normal for school sharks. When larger and more seaworthy boats are available, the local production is expected to increase sufficiently to supply Australian needs (58).

India

The shark liver oil industry in India, which had been operated on a small scale for many years, was expended during the war to fill a larger part of the needs of the country. The oil content of the shark livers is said to be 50 to 70 percent, with a potency of approximately 10,000 U. S. P. units per gram of oil. Other fishes, including the fresh-water species, have been examined as possible sources of vitamin A; but the potencies have generally been rather low. The new program for the development of the Indian fisheries includes an extensive exploitation of all possible fishery resources; and it is expected that modern methods for the capture, processing, and marketing of fish will increase the supplies of vitamin-bearing materials on which to base a larger vitamin oil industry.

Norway and Iceland

With the cessation of hostilities the Norwegian and Icelandic cod liver oil industries are again taking their normal place in the world vitamin oil field. Representatives of the two countries have mentioned plans for continuing research on improvement of quality and diversification of products from their cod fisheries and for the introduction of more modern and specialized processing equipment.

Russia

There is very little information available regarding actual production of vitamin oils in Russia; but from the reports of various scientists, it appears that an active search has been made to determine the value of the fish livers and viscera taken in the fisheries of that country. One of the scientists mentioned that the Russians were beginning to process fish livers, but no details were obtained.

(58) Anonymous, 1945. Commercial Fisherman 11, No. 21, 261.

Figure 27. Thresher shark (Alopias vulpas). Length approximately 11 feet (3.4 meters).

Figure 28. Leopard shark (Triakis semifasciatum). Length approximately 3 feet (0.9 meter).

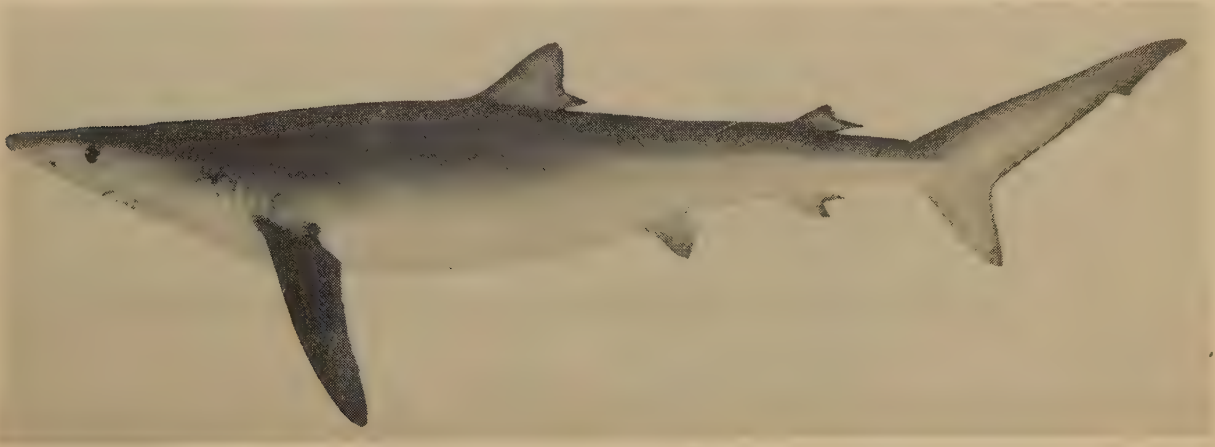

Figure 29. Great blue shark (Prionace glauca). Length approximately 8 feet (2.5 meters).

Figure 30. Bonito shark (Isurus glaucus). Length approximately 5 feet (1.5 meters).

Figure 31. Sleeper shark (Somniosus microcephelus). Length approximately 8 feet (2.5 meters).

Figure 32. Soupfin shark (Galeorhinus zyopterus). Length approximately 6 feet (1.8 meters).

Figure 33. Broadbill swordfish (Xiphias gadius). Length approximately 10 feet (3 meters).

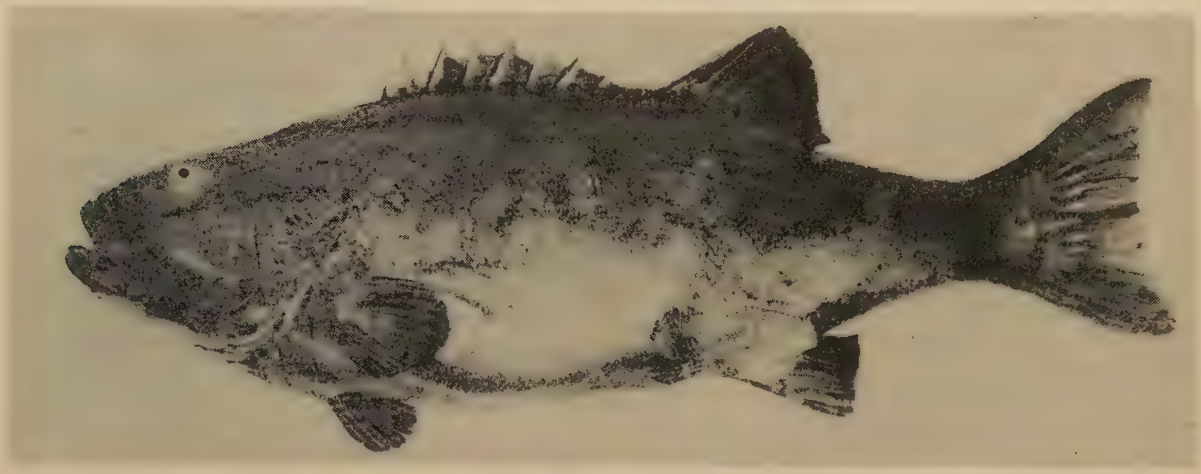

Figure 34. Black sea bass (Stereolepis gigas). Length approximately 5 feet (1.5 meters).

Figure 35. Albacore (Germo alalunga). Length approximately 3 feet (0.9 meters).

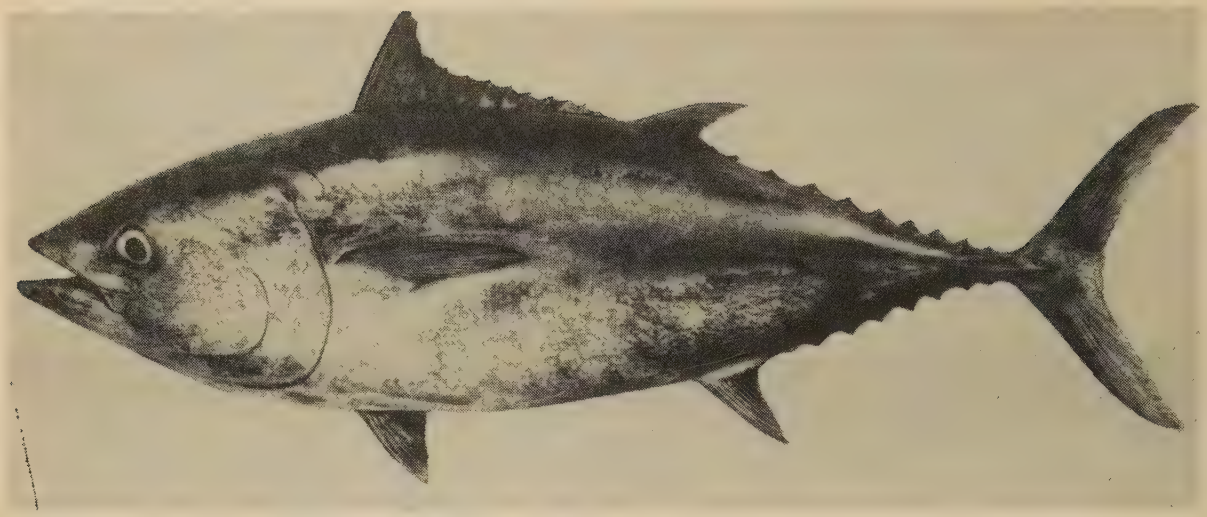

Figure 36. Bluefin tuna (Thunnus thynnus). Length approximately 3 feet (0.9 meters).

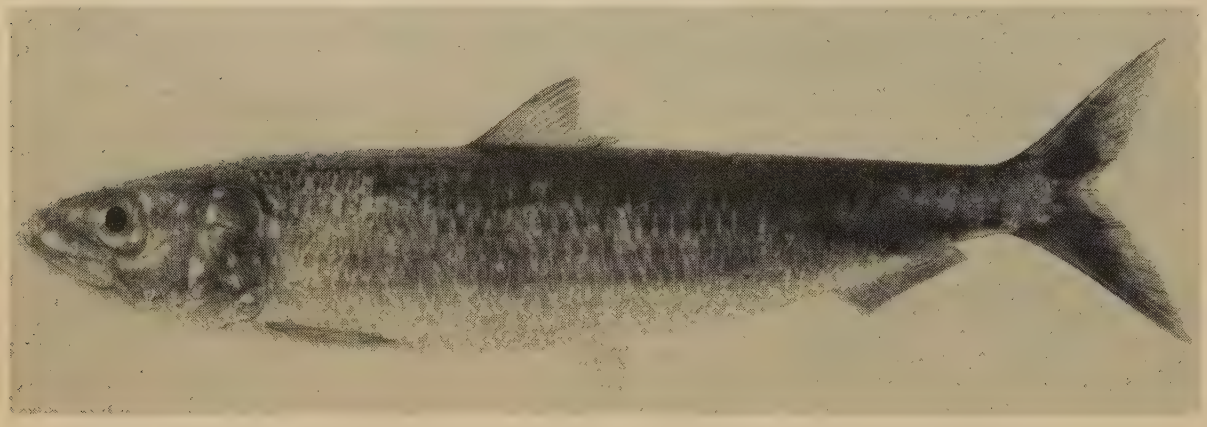

Figure 37. Pilchard (Sardina coerulea). Length approximately 10 inches (25.4 centimeters).

Figure 38. Pacific herring (Clupea pallasii). Length approximately 10 inches (25.4 centimeters).

Figure 39. Hammerhead shark (Spyrna zygaena). Length approximately 9 feet (2.75 meters).

TABLE 1. Annual Production of Vitamin-bearing fish liver oils in the United States, 1934-1945

Year	Species	Atlantic and Gulf Coasts[1]		Pacific Coast, including Alaska		Total	
		Gallons	Value	Gallons	Value	Gallons	Value
1934	Cod	94,312	$56,643	-	-	94,312	$56,643
	Miscellaneous 2/	2,526	100,872	6,073	$79,221	8,599	180,093
	Total	96,838	157,515	6,073	79,221	102,911	236,736
1935	Cod	215,479	227,019	-	-	215,479	227,019
	Miscellaneous 3/	11,605	539,687	71,773	2,799,147	83,378	3,338,834
	Total	227,084	766,706	71,773	2,799,147	298,857	3,565,853
1936	Cod	281,374	170,779	-	-	281,374	170,779
	Shark	-	-	2,860	1,010	2,860	1,010
	Miscellaneous 4/	26,526	1,099,266	40,640	1,625,600	67,166	2,724,866
	Total	307,900	1,270,045	43,500	1,626,610	351,400	2,869,655
1937	Cod	275,802	167,572	-	-	275,802	167,572
	Miscellaneous 5/	34,777	821,797	37,342	1,214,728	72,119	2,036,525
	Total	310,579	989,369	37,342	1,214,728	347,921	2,204,097
1938	Cod	261,556	164,986	-	-	261,556	164,986
	Shark	6/	6/	6/129,705	6/330,397	129,705	330,397
	Miscellaneous 7/	15,836	648,426	99,106	1,332,534	114,942	1,980,960
	Total	277,392	813,412	228,811	1,662,931	506,203	2,476,343
1939	Cod	318,069	196,296	-	-	318,069	196,296
	Shark 8/	8/	8/	8/135,467	8/845,876	135,467	845,876
	Miscellaneous 9/	19,382	828,375	205,057	2,601,141	224,439	3,429,516
	Total	337,451	1,024,671	340,524	3,447,017	677,975	4,471,688
1940	Cod	281,257	253,168	-	-	281,257	253,168
	Shark	28,018	44,780	213,084	1,087,790	241,102	1,132,570
	Tuna	9,544	642,828	217,009	2,188,963	226,553	2,831,791
	Miscellaneous 10/	7,765	295,374	33,944	575,250	41,709	870,624
	Total	326,584	1,236,150	464,037	3,852,003	790,621	5,088,153
1941	Cod	11/325,078	11/482,892	11/	11/	325,078	482,892
	Shark	41,478	1,170,665	566,411	8,030,983	607,889	9,201,648
	Tuna	7,258	548,990	158,804	1,365,160	166,062	1,914,150
	Miscellaneous 12/	17,005	1,121,975	117,208	2,150,923	134,213	3,272,898
	Total	390,819	3,324,522	842,423	11,547,066	1,233,242	14,871,588
1942	Cod	212,301	354,550	-	-	212,301	354,550
	Shark	66,172	557,119	613,123	6,563,664	679,295	7,120,783
	Tuna	616	25,550	43,780	376,989	44,396	402,539
	Other 13/	8,619	354,055	56,301	1,802,980	64,920	2,157,035
	Total	287,708	1,291,274	713,204	8,743,633	1,000,912	10,034,907
1943	Cod	133,222	189,363	-	-	133,222	189,363
	Shark	74,613	513,999	473,433	9,418,475	548,046	9,932,474
	Tuna 14/	14/	14/	26,823	1,305,146	26,823	1,305,146
	Miscellaneous 15/	16,030	49,976	127,733	3,365,011	143,763	3,414,987
	Total	223,865	753,338	627,989	14,088,632	851,854	14,841,970
1944	Cod	82,619	123,796	-	-	82,619	123,796
	Shark	85,489	614,869	711,368	9,004,496	796,857	9,619,365
	Tuna	703	20,430	39,102	1,428,025	39,805	1,448,455
	Miscellaneous 16/	1,638	45,471	56,004	1,983,292	57,642	2,028,763
	Total	170,449	804,566	806,474	12,415,813	976,923	13,220,379
1945	Cod	122,796	253,603	-	-	122,796	253,603
	Shark	98,545	429,917	448,234	6,092,992	546,779	6,522,909
	Tuna	17/	17/	17/51,399	17/1,576,922	51,399	1,576,922
	Miscellaneous 18/	21,407	452,775	61,907	2,395,998	83,314	2,848,773
	Total	242,748	1,136,295	561,540	10,065,912	804,288	11,202,207

1/ Includes the production of burbot liver oil in Minnesota and Wisconsin.
2/ Includes halibut and burbot liver oils from the Atlantic Coast and miscellaneous liver oils from the Pacific Coast (from original data not segregated in the annual summary).
3/ Partly estimated.
4/ Includes burbot, halibut, sablefish, swordfish, tuna, "lingcod", and totuava liver oils.
5/ Includes burbot, halibut, sablefish, swordfish, tuna, shark, and miscellaneous liver oils.
6/ Production from Massachusetts and Florida included in Pacific Coast data.
7/ Includes burbot, halibut, sablefish, swordfish, tuna, and miscellaneous liver oils. A small quantity of halibut viscera oil has been included with the Pacific Coast production of miscellaneous liver oils.
8/ Shark-liver oil production in Florida included under Pacific Coast.
9/ Includes burbot, flounder, halibut, "lingcod", mackerel, sablefish, swordfish, tuna, and miscellaneous liver oils.
10/ Includes burbot, halibut, mackerel, sablefish, swordfish, and miscellaneous liver oils on the Atlantic Coast, and flounder, halibut, sablefish, and miscellaneous liver oils on the Pacific Coast.
11/ A small quantity of cod-liver oil produced in Washington has been included with the production of cod-liver oil on the Atlantic Coast.
12/ Includes burbot, halibut, sablefish, mackerel, swordfish, and miscellaneous liver oils on the Atlantic Coast and flounder, halibut, sablefish, mackerel, and miscellaneous livef oils on the Pacific Coast.
13/ Includes the production of burbot, swordfish, and mixed liver oils on the Atlantic Coast and mixed liver oils on the Pacific Coast.
14/ The production of tuna-liver oil in Massachusetts has been included with the production of that item on the Pacific Coast.
15/ Includes burbot, swordfish, mixed liver, and industrial cod liver oils on the Atlantic Coast and flounder, halibut, sablefish, and mixed liver oils from the Pacific Coast.
16/ Includes burbot, swordfish, halibut, and mixed-liver oils on the Atlantic Coast and flounder, halibut, "lingcod", rock cod, rockfish, sablefish, and mixed-liver oils on the Pacific Coast.
17/ A small quantity of tuna liver oil produced on the Atlantic Coast has been included with the production on the Pacific Coast.
18/ Includes the production of burbot, swordfish, halibut, and mixed-liver oil on the Atlantic Coast and flounder, halibut, "lingcod", rockfish, sablefish, and mixed-liver and viscera oils on the Pacific Coast.

TABLE 2. Relative Importance of Fish Liver Oils in the United States from Principal Species in 1943

Species	Liver Oil Produced	
	Gallons	Value
Miscellaneous shark	428,972	$8,071,448
Soupfin shark	43,211	2,094,592
Tuna	26,735	1,284,222
Halibut	10,273	915,492
"Lingcod"	2,861	485,264
Grayfish (dogfish)	35,743	226,820
Cod	133,222	189,363
Sablefish	329	19,088
Rockfish	192	14,761
Miscellaneous 1/, Pacific Coast	77,641	955,917
Miscellaneous 2/, Atlantic Coast	90,886	591,691
Totals	850,065	$14,848,658

1/ Includes halibut and sablefish visceral oils, sole and mixed liver oils.
2/ Includes burbot, swordfish, halibut and miscellaneous liver oil.

Table 3 - Vitamin A Content of Oils from Fishery Sources having Commercial Importance in the United States & Alaska 1/

Common name	Scientific name	Area in which fish are caught	Source of oil	Percent of round weight 2/	Oil content, percent	Vitamin A content in U. S. Pharmacopoeia units per gram of oil		
						Range		Average
Soupfin shark	Galeorhinus zyopterus	Pacific (male)	liver	10	55-68	45,000-	200,000	120,000
" "	" "	" (female)	"	10	65-72	15,000-	40,000	32,000
Grayfish (dogfish)	Squalus suckleyi	" -Alaska	"	10	67-72	2,000-	20,000	5,000
" "	" "	" -Hecate Strait	"	10	65-70	7,000-	15,000	10,000
" "	" "	" -Wash.-Ore.	"	10	50-70	8,000-	25,000	14,000
		" -N. Calif.	"	10	62-68	12,000-	20,000	15,000
Halibut	Hippoglossus hippoglossus	Pacific-Area 3/	liver	1.5-3	8-21	40,000-	160,000	87,000
"	" "	" - " 4/	"	1 -1.75	17-27	20,000-	65,000	40,000
"	" "	"	viscera 5/	2.5-5	2-5	70,000-	700,000	200,000
Sablefish	Anoplopoma fimbria	Pacific	liver	2 -2.5	10-26	50,000-	190,000	90,000
"	" "	"	viscera	3 -4	5-12	90,000-	250,000	125,000
Lingcod	Ophiodon elongatus	Pacific	liver	1 -1.5	8-20	40,000-	550,000	175,000
"	" "	"	viscera	1.8-3	4-15	10,000-	175,000	40,000
Sleeper shark	Somniosus microcephalus	Pacific	liver	10 -15	40-55	5,000-	15,000	7,000
Mud shark	Hexanchus griseus	"	"	10 -15	60-65	5,000-	7,000	5,500
Great blue shark	Priomace glauca	"	"	6/	30-45	7,000-	27,000	20,000
Hammerhead shark	Sphyrna zygaena	" -Atlantic	"	6/	30-40	30,000-	120,000	50,000
" "	" diplana	"	"	6/	55-75	20,000-	150,000	60,000
" "	" "	Atlantic	"	6/	6/	5,000-	140,000	40,000
" "	" tudes	Florida	"	6/	6/	10,000-	125,000	50,000
Little black tip	Isogomphodon maculipinnis	Florida	"	6/	40-60	5,000-	25,000	5,000
Tiger shark	Galeocerdo arcticus	"	"	6/	45-60	2,000-	5,000	3,000
Sand-bar shark	Carcharinus milberti	"	"	6/	6/	3,000-	15,000	8,000
Nurse shark	Giglymostoma cirratum	"	"	6/	6/	1,000-	10,000	3,000
Dusky shark	Carcharinus obscurus	"	"	6/	6/	5,000-	60,000	25,000
Leopard shark	Triakis semifasciatum	Pacific	"	6/	40-50	1,000-	5,000	3,000
Bay shark	Carcharias lamiella	"	"	6/	60-75	2,000-	20,000	10,000
Thresher shark	Alopias vulpas	"	"	6/	45-55	1,000-	5,000	3,000
Mexican shark	Eulamia lamiella	"	"	6/	40-50	20,000-	80,000	40,000
Gray smooth hound	Mustelatus californicus	"	"	6/	50-60	10,000-	25,000	20,000
Cazon shark	Unknown	Argentina-Brazil	"	7 -10	30-45	10,000-	200,000	50,000
Albacore tuna	Germo alalunga	Pacific	"	1.5-2	7-20	10,000-	60,000	25,000
Bluefin tuna	Thunnus thynnus	"	"	6/	4- 6	25,000-	100,000	75,000
Yellowfin tuna	Neothunnus macropterus	"	"	6/	3- 5	35,000-	90,000	50,000
Skipjack tuna	Euthynnus pelayms	"	"	6/	4- 6	30,000-	60,000	40,000
Bonito	Sarda chiliensis	"	"	6/	4-12	15,000-	60,000	35,000
Swordfish	Xyphias gladius	Pacific-Atlantic	"	1.4-2.6	8-35	20,000-	400,000	250,000
"	" "	" "	viscera	3 -6	6-12	2,000-	30,000	10,000
Black sea bass	Stereolepis gigas	Pacific	liver	6/	13-20	100,000-	1,000,000	300,000

(Continued on the following page)

Table 3 - Vitamin A Content of Oils from Fishery Sources having Commercial Importance in the United States & Alaska[1/] (Cont.)

Common name	Scientific name	Area in which fish are caught	Source of oil	Percent of round weight[2/]	Oil content, percent	Vitamin A content in U. S. Pharmacopoeia units per gram of oil	
						Range	Average
Totuava	Cynoscion nobilis	Pacific	liver	6/	15-25	40,000-400,000	6/
Cod	Gadus callarias	Atlantic	"	3 -5	20-60	1,000- 6,000	2,000
Rosefish	Sebastes marinus	"	waste[7/]	6/	2-4	3,000- 5,000	6/
Halibut	Hippoglossus hippoglossus	"	liver	1.5-2.5	15-25	40,000	6/
Rockfish	Sebastodes	Pacific	"	1 -1.5	5-25	14,000-300,000	6/
"	"	"	viscera	1.5-2.5	2-15	15,000-125,000	6/
Petrale sole	Eopsetta jordani	Pacific	liver	1 -1.5	6-25	4,000-175,000	6/
Herring	Clupea pallasii	"	body	6/	5-25	50- 300	90
Pilchard	Sardina caerulea	"	"	6/	5-25	50- 800	100
Menhaden	Brevoortia tyrannus	Atlantic	"	6/	5-20	500	6/

1/ These data compiled from reports of research at the laboratories of the Fish and Wildlife Service and of the Fisheries Research Board of Canada, and from articles published by representatives of commercial processors of fish livers and viscera. For the most part, the data are based on large lots of material or on samples taken over the normal season for the species. Vitamin D data for some of these species are included in Table 3.

2/ Percent of round weight means the proportion of liver weight to the weight of the entire fish (undressed) expressed as percent.

3/ Area 3 is defined by the International Halibut Commission regulations as follows: "Area 3 shall include all the convention waters off the coast of Alaska that are between Area 2 and a straight line running south from the southwestern extremity of Cape Sagak on Umnak Island, at a point approximately latitude 52° 49' 30" N., longitude 169° 07' 00" W., according to Chart 8802, published January, 1942, by the United States Coast and Geodetic Survey, and that are south of the Alaska Peninsula and of the Aleutian Islands and shall also include the intervening straits or passes of the Aleutian Islands."

4/ Area 2 includes: "all convention waters off the coasts of the United States of America and of Alaska and of the Dominion of Canada between Area 1B and a line running through the most westerly point of Glacier Bay, Alaska, to Cape Spencer Light as shown on Chart 8304, published in June, 1940, by the United States Coast and Geodetic Survey, which light is approximately latitude 58° 11' 57" N., longitude 136° 38' 18" W., thence south one-quarter east and is exclusive of the areas closed to all halibut fishing in Section 9 of these regulations."

5/ Viscera, unless otherwise designated, means the contents of the body cavity minus the liver, stomach, and gonads.

6/ The source from which information listed here was obtained did not supply data under this heading.

7/ Waste is the entire body of the rosefish minus the fillet or edible portion. It includes head, backbone, skin, and viscera.

Table 4 - Vitamin A Content of Oils from Fishery Sources having Little or No Present Commercial Importance in the U.S. & Alaska[1/]

Common name	Scientific name	Area in which fish are caught	Source of oil	Percent of round weight[2/]	Oil content, percent	Vitamin A content in U. S. Pharmacopoeia units per gram of oil
Basking shark	Cetorhinus maximus	Pacific	liver	3/	60-70	300
Spotted cow shark	Notorynchus maculatus	"	"	6	29	1,400
Cod	Gadus macrocephalus	"	"	1.5-4	25-45	5,000- 17,000
"	" "	"	viscera[4/]	3.2-3.6	1.4-2.6	36,000-112,000
Cabrilla	Epinephelus analogus	"	liver	3/	13	164,000
Cormuda	Unknown	"	"	3/	50	30,000
Pejerala	"	"	"	3/	27	98,000
Yellowtail	Seriola dorsalis	"	"	3/	5-7	20,000- 40,000
Arrow-tooth halibut	Atheresthes stomias	"	"	3/	10-15	10,000- 80,000
English sole	Parophrys vetulus	"	"	1 -1.5	5-10	5,000
Starry flounder	Platichthys stellatus	"	"	1.5-2	10-15	1,000- 25,000
King salmon	Oncorhynchus tschawytscha	"	"	3/	4-8	10,000- 40,000
" "	" "	"	offal[5/]	30	10-15	1,500- 2,000
Sockeye "	" nerka	"	liver	1.5-2	5-8	10,000- 50,000
" "	" "	"	offal	33	10-20	500- 5,000
Silver "	" kisutch	"	liver	1.5-2.5	4-6	10,000- 30,000
" "	" "	"	offal	33	10-15	500- 3,000
Pink "	" gorbuscha	"	liver	3/	4-6	1,000- 40,000
" "	" "	"	offal	35	10-12	500- 3,000
Chum "	" keta	"	liver	1.5-2.5	2-6	5,000- 15,000
" "	" "	"	offal	33	5-10	none
Steelhead	Salmo gairdneri	"	liver	3/	10-20	10,000- 20,000
Skate	Raja binoculata	"	"	3/	30-60	500- 3,000
Starry skate	" stellulata	"	"	3/	10-30	4,000- 30,000
Ratfish	Hydrolagus colliei	"	"	3/	70-85	100- 1,000
Finback whale	Balaenoptera velefera	"	"	3/	0.8	40,000
Sperm whale	Physeter macrocephalus	"	"	3/	1.0	440,000
Beluga "	Delphinapterus leucas	"	"	3/	0.3	10,000
Stockfish	Merlucius capensis (Castel.)	South Africa	"	2.5-4	28-50	6,000- 28,000
"	" " "	" "	viscera	0.7-1.0	2.5-3.5	80,000-650,000
Kingklip	Genypterus capensis (Smith)	" "	liver	1.3-3.3	25-45	7,000- 52,000
"	" " "	" "	viscera	2.0	1-2	10,000- 32,000
Kabeljou	Sciaena hololepidota (Lacep.)	" "	liver	3/	25	85,000
Stone-bass	Polyprion americanus (Bl. & Schn.)	" "	"	1.6	10-20	75,000-700,000
Blue shark	Unknown	" "	"	3/	3/	15,000- 30,000
Dogfish	"	" "	"	3/	3/	4,000- 6,000
John Dory	Zeus capensis (C. & V.)	" "	"	4 -5	13-37	8,000- 44,000
" "	" " "	" "	viscera	3 -3.5	1-5	20,000-100,000

(Continued on the following page)

Table 4 - Vitamin A Content of Oils from Fishery Sources having Little or No Present Commercial Importance in the U.S. & Alaska[1/] (Continued)

Common name	Scientific name	Area in which fish are caught	Source of oil	Percent of round weight[2/]	Oil content, percent	Vitamin A content in U. S. Pharmacopoeia units per gram of oil
Halibut	Unknown	South Africa	liver	3/	3/	50,000
Cod	"	" "	"	3/	3/	1,000
Snoek	Thyrsites atun (Euphrasen)	" "	"	1.5	16.5	14,000-560,000
"	" " "	" "	viscera	1.6	11.7	20,000-160,000
Horse mackerel	Trachurus trachurus, Lin.	" "	liver	1.25-2.75	5-15	80,000-600,000
" "	" " "	" "	viscera	1.25-3	2-15	20,000-130,000
Bonito	Isurus glaucus	Florida	liver	3/	40-50	500- 1,500
Mackerel shark	Carcharinus platyodon	"	"	3/	3/	2,000- 4,500
Black-nose shark	" scronotus	"	"	3/	3/	1,200
No-name shark	" falciformis	"	"	3/	3/	6,600
Silky shark	" floridanus	"	"	3/	3/	2,000- 5,000
Bonnet-head	Sphyrna tiburo	"	"	3/	3/	900
Great white shark	Carcharodon carcharias	"	"	3/	3/	700- 7,000
Spotted eagle ray	Stoasodon narinari	"	"	3/	3/	35
Cow-nosed ray	Rhinoptera bonasus	"	"	3/	3/	675
Manta	Manta birostris	"	"	3/	3/	200- 400
Sawfish	Pristis pectinatus	"	"	3/	3/	900- 7,000
Congrio negro	Genyoterus chilensus	Chile	"	3/	3/	1,000- 2,000
Cow shark	Unknown	"	"	3/	54-70	1,600- 3,000
Raya	"	"	"	3/	30	13,000
Barn-door skate	"	"	"	3/	52	4,000
Tollo	Galeorhinus mento	"	"	3/	20-53	1,200- 87,000
Peje-gallo	Callorhynchus callorhynchus	"	"	3/	28-41	700- 1,600
Pinta roja	Unknown	"	"	3/	7-41	1,300- 4,600
Spiny dogfish	"	"	"	3/	41-46	6,000- 14,000
Six-gill shark	"	"	"	3/	85	1,500
Bacalao	Polyprion oxigensis	"	"	3/	0.3-5.4	16,000-425,000
Sierra	Thysitops lepidopoides	"	"	3/	0.8	208,000
Unknown shark	Galeorhinus	"	"	3/	57	49,000
Merluza	Unknown	"	"	3/	25-37	3,000- 4,000
Hammerhead shark	Sphyrna zygaena	Brazil	"	3/	3/	175,000-200,000
Unknown	Carcharias limbatus	"	"	3/	3/	50,000-125,000
"	" lamia	"	"	3/	3/	50,000
"	Odontaspis americanus	"	"	3/	3/	10,000- 50,000
"	Isurus oxyrhynchus	"	"	3/	3/	25,000
"	Rhinoptera jussieuri	"	"	3/	3/	3,000- 5,000
"	Galeocerdo maculatus	"	"	3/	3/	1,000- 3,000
"	Manta chrenbergii	"	"	3/	3/	3,000- 5,000

(Continued on the following page)

Table 4 - Vitamin A Content of Oils from Fishery Sources having Little or No Present Commercial Importance in the U.S. & Alaska[1/] (Continued)

Common name	Scientific name	Area in which fish are caught	Source of oil	Percent of round weight[2/]	Oil content, percent	Vitamin A content in U. S. Pharmacopoeia units per gram of oil
Sardinero	Eulamia aethalorus	Pacific-Mexico	liver	3/	66-78	3,000- 16,000
Gambruso	" azureus	" "	"	3/	68	17,500
Pilota	" galapagensis	" "	"	3/	32-55	8,000-110,000
Puro	" velox	" "	"	3/	69-79	20,000- 30,000
"	Scoliodon longurio	" "	"	3/	68	50,000
Unknown shark	Unknown	India	"	3/	50-70	8,000- 12,000
Sawfish	Pristis pectinatus	"	"	3/	3/	12,000
Unknown	Scoliodon palasorrah	Philippines	"	3/	5	2,000
Sawfish	Pristis microdon, Lothan	"	"	3/	8	300
Sanga	Mobula enegeodoo-tenke	"	"	3/	3/	2,400
Unknown	Mustelus canis, Mitch.	Uruguay	"	3/	3/	50,000- 60,000
"	Micropogon ondulatus	"	"	3/	3/	20,000- 50,000
Corvina	Unknown	"	"	3/	3/	20,000
Pescadilla	Cynoscian	"	"	3/	3/	25,000
Dogfish	Squalus acanthias	Atlantic	"	3/	40-60	1,000- 7,000
Yellowtail	Seriola dorsalis	Australia	"	3/	3/	42,000
Congrio colorado	Genypterus blacodes	"	"	3/	3/	1,000- 2,000
Ling	" "	New Zealand	"	3/	35	16,000- 24,000

1/ Vitamin D data for some of these species are included in Table 3.
2/ Percent of round weight means the proportion of liver weight to the weight of the entire fish (undressed) expressed as percent.
3/ The source from which information listed here was obtained did not supply data under this heading.
4/ Viscera indicates the contents of the body cavity minus stomach, liver, and gonads.
5/ Offal indicates cannery trimmings, including head and viscera.

Table 5 - Vitamin D Content of Oils from Fishery Sources

Common name	Scientific name	Area in which fish are caught	Source of oil	Vitamin D content in International units per gram of oil
Albacore tuna	Germo alalunga	Pacific	liver	25,000-250,000
Bluefin "	Thunnus thynnus	"	"	20,000- 70,000
Yellowfin "	Neothunnus macropterus	"	"	10,000- 45,000
Skipjack "	Euthynnus pelayms	"	"	25,000-250,000
Bonito	Sarda chiliensis	"	"	50,000
Swordfish	Xyphias gladius	" -Atlantic	"	2,000- 25,000
Mackerel, Pacific	Scomber diego	Pacific	"	1,400
Albacore tuna	Germo alalunga	"	waste 2/	67
Halibut	Hippoglossus hippoglossus	"	liver	1,000- 5,000
"	" "	"	viscera 3/	100- 500
Sablefish	Anaplopoma fimbria	"	liver	600- 1,000
"	" "	"	viscera	100
Lingcod	Ophiodon elongatus	"	liver	1,000- 6,000
"	" "	"	viscera	100- 200
Rockfish	Sebastodes sp.	"	liver	300- 5,000
Cod	Gadus macrocephalus	"	"	85- 500
Ishinagi	Stereolepis	"	"	3,800
Barracuda	Sphyraena argentes	"	"	2,000
Black sea bass	Stereolepis gigas	"	"	5,000
Beluga whale	Delphinapterus leucas	"	"	50- 100
Grayfish (Dogfish)	Squalus suckleyi	"	"	5- 25
" "	" "	"	body 4/	29
Ratfish	Hydrolagus colliei	"	liver	2- 5
Soupfin shark	Galeorhinus zyopterus	"	"	5- 25
Herring	Clupea pallasii	"	body 5/	25- 160
"	" "	"	liver	250
Pilchard	Sardina caerulea	"	body 5/	20- 100
King salmon	Oncorhynchus tschawytscha	"	liver	100- 500
" "	" "	"	offal 6/	50- 150
Sockeye "	" nerka	"	liver	200- 600
" "	" "	"	offal	100- 300
Silver "	" kisutch	"	liver	100- 500
" "	" "	"	offal	100- 200
Pink "	" gorbuscha	"	liver	100- 600
" "	" "	"	offal	100- 300
Chum "	" keta	"	liver	100- 500
" "	" "	"	offal	50- 100
Starry flounder	Platichthys stellatus	"	liver	1,000
Rex sole	Errex zachirus	"	"	150
Skate	Raja binoculata	"	"	25
Mud shark	Hexanchus griseus	"	"	20
Snoek	Thyrsites atun (Euphrasen)	South Africa	"	500- 6,000
"	" " (")	" "	viscera	85
Stonebass	Polyprion americanus (Bl. & Schn.)	" "	liver	700- 1,300
Stockfish	Merlucius capensis (Castel.)	" "	"	50- 380
"	" " (")	" "	viscera	3
Kingklip	Genypterus " (Smith)	" "	liver	85- 600
Halibut	Unknown	" "	"	1,000- 2,000
Cod	"	" "	"	100
Ling	Genypterus blacodes	New Zealand	"	500
Yellowtail	Seriola dorsalis	Australia	"	9,000- 17,000
Halibut	Hippoglossus hippoglossus	Atlantic	"	2,000
Mackerel, common	Scomber scombrus	"	"	750
Rosefish	Sebastes marinus	"	waste 7/	50
Dogfish	Squalus acanthias	"	liver	3

1/ Data on vitamin A content of most of these fish are to be found in Tables 1 and 2.
2/ Waste indicates offal from the cannery fish cleaning tables. The raw eviscerated fish is pre-cooked prior to this cleaning operation, hence some of the tuna body oil has been lost from this waste before it is made into meal and oil.
3/ Viscera indicates the contents of the body cavity minus the liver, stomach, and gonads.
4/ Body indicates the entire body of the fish minus the liver.
5/ Body indicates the entire body of the fish including the liver and viscera.
6/ Offal indicates the cannery trimmings, including heads, livers and viscera but not eggs.
7/ Waste indicates the entire body of the rosefish minus the fillet or edible portion. It includes head, backbone, skin, and viscera.

TABLE 6. Annual Importations of Fish Livers and Vitamin-bearing Fish Liver Oils into the United States, 1934-1945.

Year	Cod		Shark		Miscellaneous Liver Oils		Miscellaneous Fish Livers	
	Gallons	Value	Gallons	Value	Gallons	Value	Pounds	Value
1934	3,470,259	$2,190,985	-	-	1/1,624	$42,563	-	-
1935	4,607,093	2,975,298	-	-	1/1,662	23,587	-	-
1936	5,789,574	3,546,733	-	-	-	-	-	-
1937	5,915,964	3,866,971	-	-	-	-	2,473,962	$421,141
1938	5,228,637	3,326,496	-	-	-	-	4,931,580	658,057
1939	6,670,274	3,730,985	2/9,572	$6,773	1/ 2	50	6,254,873	1,717,945
1940	3,114,392	2,521,239	2/65,135	38,218	-	-	8,443,877	2,462,085
1941	1,695,841	2,945,877	2/367,887	587,374	101,467	314,393	4,943,666	1,221,841
1942	636,836	1,299,874	2/173,353	426,231	1,404	47,245	3,751,042	1,631,559
1943	1,804,467	3,504,293	144,674	502,239	261,346	1,469,803	4,004,088	2,201,129
1944	1,695,461	2,919,091	36	116	61,036	4,065,834	4,709,774	2,376,179
1945	1,768,015	2,891,707	82,382	155,018	53,686	5,347,320	4,150,946	1,544,341

1/ Halibut liver oil.
2/ Shark body oil and shark liver oil.

Source: Foreign Commerce and Navigation of the United States, U. S. Department of Commerce.